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CHROMONES

Part II. Molecular Rearrangement of *o*-Acyloxyacetoarones: Synthesis of Chromones

By V. V. Virkar and R. C. Shah, F.A.Sc.

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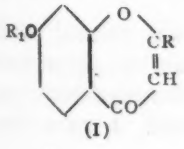
Received October 28, 1948

In the previous work by Virkar and Wheeler,[1] Virkar and Shah,[2] and Virkar[3] it has been been shown that metallic sodium is a new and better reagent for the transformations of *o*-benzoyloxy-, *o*-naphthoyloxy-, or *o*-nitrobenzoyloxy-acetoarones to the corresponding *o*-hydroxydiaroylmethanes. It has now been observed that metallic sodium can be conveniently used even for the transformations of *o*-acetoxyacetoarones, which finally give 3-acyl-2-alkyl-chromones or 2-alkyl-chromones. It may be pointed out that no transformation has been observed with 2-acetoxyacetoarones except some attempts by Baker[4] who was unable to transform resacetophenone-diacetate and 4-*o*-benzoyl-2-*o*-acetylresacetophenone using potassium carbonate. Transformations of these two, as well as some other *o*-acetoxyacetoarones have now been achieved using metallic sodium, thus providing a new method for the synthesis of chromones.

o-Acetoxyacetophenone, when treated with metallic sodium gave a mixture of (*o*-hydroxy)-benzoylacetone and another product which appeared to be 2-methyl-3-acetylchromone. The former on cyclisation gave 2-methyl-chromone. 2: 6-Diacetoxy-acetophenone on similar treatment gave directly 5-hydroxy-2-methyl-3-acetylchromone. As is the case with the dibenzoyloxy derivative,[1, 4] here also the intermediate triketone could not be isolated.

2: 4-Diacetoxyacetophenone and 2-acetoxy-4-benzoyloxyacetophenone by the above method, afforded 7-hydroxy-2-methyl-3-acetyl- and 7-hydroxy-2-methyl-chromones respectively. 2-Acetoxy-4-methoxyacetophenone with metallic sodium furnished three products, *viz.*, (2-hydroxy-4-methoxy)-benzoylacetone (II: $R = R_1 = CH_3$), 7-methoxy-2-methyl-3-acetylchromone (III: $R = R_1 = CH_3$), and 7-hydroxy-2-methylchromone (I: $R = CH_3$, $R_1 = H$). The benzoylacetone on cyclisation gave 7-methoxy-2-methyl-chromone (I: $R = R_1 = CH_3$).



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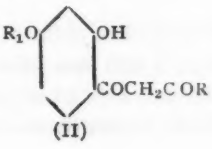

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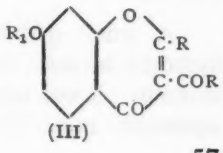

(III)

This molecular rearrangement of 2-acetoxy-4-methoxy-acetophenone is a singular case inasmuch as all the three products, *viz.*, a diketone (II), a chromone (I) and a 3-acylchromone (III) expected to be formed according to the mechanism as advanced by Baker,[4] have been isolated in one and the same reaction. This observation lends experimental proof to the views advanced by Baker. The formation of 7-hydroxy-2-methylchromone is the first instance observed where metallic sodium has acted as a demethylating agent apart from bringing about the transformation and cyclisation.

Experimental

Molecular Rearrangement of o-Acetoxyacetophenone: o-Hydroxybenzoylacetone

A mixture of *o*-acetoxyacetophenone (3 g.), pulverised sodium (0·35 g.) and dry benzene (10 c.c.) was refluxed for 3 hours. Benzene was distilled, the yellow residue treated with alcohol and then acidified with dilute hydrochloric acid. The oil that separated was extracted with ether and the extract shaken with copper acetate solution. The ethereal layer was removed and the copper salt that had separated in copper acetate solution was filtered and washed with ether. As it could not be crystallised, it was decomposed by shaking with dilute hydrochloric acid and ether. The ether layer was separated, dried and ether evaporated. The viscous mass that remained solidified after sometime in frigidaire. (*o*-Hydroxy)-benzoylacetone was crystallised from petroleum ether containing little alcohol into pale yellow plates, m.p. 102° C. (poor yield). (Found: C, 67·3; H, 5·8. Calculated for $C_{10}H_{10}O_3$: C, 67·4; H, 5·6 per cent.) Wittig[5] gives m.p. 90·5°–91·5° C. It gave reddish coloration with alcoholic ferric chloride.

The ethereal solution, after removal of the copper salt, was washed with dilute alkali and water and then dried. The pasty residue, obtained on evaporation of ether, was dissolved in excess of light petroleum (40°–60° C.) and kept in frigidaire when after about 24 days a white compound separated, m.p. 78°–82° C. It did not give coloration with alcoholic ferric chloride or fluorescence with concentrated sulphuric acid. It appeared to be 2-methyl-3-acetylchromone for which Wittig[5] gives m.p. 88·5°–89·5° C. However, the quantity of the isolated compound was insufficient for further investigation.

2-Methylchromone

A small quantity of (*o*-hydroxy)-benzoylacetone was treated with hydrogen bromide in acetic acid and was allowed to remain for about half an hour. It was then diluted and kept in frigidaire when 2-methylchromone separated, m.p. 71° C. With concentrated sulphuric acid it gave blue

fluorescence. Bloch and Kostanecki[6] prepared it from (2-methoxybenzoyl) acetone and give m.p. 70°–71° C.

Molecular Rearrangement of 2: 6-*Diacetoxyacetophenone:* 5-*Hydroxy-2-methyl-3-acetylchromone*

2: 6-Diacetoxyacetophenone (3·5 g.) and pulverised sodium (0·46 g.) in dry benzene (30 c.c.) were heated under reflux for three hours. Benzene was removed from the reaction mixture, the residue treated with alcohol and then with dilute hydrochloric acid. The product was crystallised from dilute alcohol, when 5-hydroxy-2-methyl-3-acetylchromone separated as colourless crystals, m.p. 121° C. (74% yield). Limaye and Kelkar[7] prepared it by Kostanecki-Robinson reaction on 2-acetylresorcinol and give m.p. 122° C. Acetyl derivative, crystallised from water, m.p. 109° C. Limaye and Kelkar[7] give m.p. 109° C.

Molecular Rearrangement of 2: 4-*Diacetoxyacetophenone:* 7-*Hydroxy-2-methyl-3-acetylchromone*

Pulverised sodium (1·3 g.), 2: 4-diacetoxyacetophenone (11·8 g.) and dry benzene (50 c.c.) were refluxed for five hours and the separated sodium salt collected, washed with benzene and treated with alcohol. It was then acidified with dilute hydrochloric acid and 7-hydroxy-2-methyl-3-acetylchromone that separated crystallised from dilute alcohol, white plates m.p. 182° C. (45% yield). Tahara[8] gives m.p. 182° C.; Kostanecki and Rozycki[9] give m.p. 182°–84° C. Acetyl derivative, m.p. 127°–28° C.; Tahara[8] gives m.p. 127° C. Benzoyl derivative, m.p. 167° C.; Kelkar and Limaye[10] give the same melting point.

Molecular Rearrangement of 2-*Acetoxy*-4-*benzoyloxyacetophenone:* 7-*Hydroxy-2-methylchromone*

To pulverised sodium (1·1 g.) in dry benzene (50 c.c.) was added 2-acetoxy-4-benzoyloxyacetophenone (8 g.) and the mixture refluxed for three hours. The reaction mixture was worked up as in the previous cases when after crystallisation from alcohol (charcoal) 7-hydroxy-2-methylchromone, m.p. 249° C., was obtained (47% yield); Tahara[8] gives m.p. 250° C.; Bloch, and Kostanecki[11] give m.p. 249°–50° C. Acetyl derivative, m.p. 94° C.; Kostanecki and Rozycki[9] give m.p. 94°–95° C.

Molecular Rearrangement of 2-*Acetoxy*-4-*methoxyacetophenone*

2-Acetoxy-4-methoxyacetophenone (20 g.), pulverised sodium (2·3 g.) and dry benzene (40 c.c.) were heated for three hours, and the reaction mixture on working up gave brownish viscous mass which on cooling turned semisolid.

On treating with alcohol a yellowish solid separated. It was crystallised from alcohol, shining pale yellow plates, m.p. 162° C. (poor yield). It was insoluble in cold dilute alkali, gave no alcoholic ferric chloride coloration and no fluorescence with concentrated sulphuric acid. Hence it appeared to be 7-methoxy-2-methyl-3-acetylchromone. Tahara[8] records m.p. for the same as 160° C.

The alcoholic solution after removing 7-methoxy-2-methyl-3-acetylchromone was diluted, the oil separated extracted with ether, the extract washed and shaken with copper acetate solution when the copper salt of β-diketone separated. It was decomposed with hydrochloric acid in ether suspension, the ether layer separated washed and dried. (2-Hydroxy-4-methoxy)-benzoylacetone obtained on evaporation of ether was crystallised from alcohol, yellowish brown needles, m.p. 75° C. (poor yield). (Found: C, 63·3; H, 6·0. Calculated for $C_{11}H_{12}O_4$. C, 63·5; H, 5·8 per cent.). Nagai[13] gives m.p. 68° C.

The ethereal extract after removal of the copper salt of the β-diketone was washed and shaken with dilute sodium hydroxide solution. The alkali layer on acidification gave a product which when crystallised from alcohol melted at 248°–49° C. (traces). It gave violet fluorescence with concentrated sulphuric acid. This showed that the compound was 7-hydroxy-2-methylchromone. Bloch and Kostanecki[6] give m.p. 249°—50° C.

7-Methoxy-2-methylchromone

A solution of 2-hydroxy-4-methoxybenzoylacetone (0·1 g.) in glacial acetic acid (1 c.c.) was treated with hydrogen bromide in acetic acid (1 c.c.) and kept at room temperature for some time. Most of the acetic acid was then removed by evaporation and then the reaction mixture diluted with water. After some time in frigidaire it gave long tiny needles of 7-methoxy-2-methylchromone, m.p. 113°–14° C. Nagai[12] and Kostanecki and Rozycki[9] give the same melting point.

Summary

In the previous work it has been shown that metallic sodium is a better reagent for the transformation of *o*-aroyloxyacetoarones to the corresponding *o*-hydroxydiaroylmethanes. It has now been observed that metallic sodium can be conveniently used even for the transformations of *o*-acyloxyacetoarones which finally give 3-acyl-2-alkylchromones or 2-alkylchromones. Thus *o*-acetoxyacetophenone when treated with metallic sodium in dry toluene gave (*o*-hydroxybenzoyl) acetone which on cyclisation gave 2-methylchromone. 2: 6-Diacetoxy-, 2: 4-diacetoxy-, and 2-acetoxy-4-benzoyloxy-

acetophenones on similar treatment gave directly the corresponding chromones. 2-Acetoxy-4-methoxyacetophenone gave all the three products expected according to the mechanism given by Baker, *viz.*, 2-hydroxy-4-methoxybenzoylacetone, 7-methoxy-2-methyl-3-acetylchromone and 7-hydroxy-2-methylchromone.

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CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part IX. Some Lichens on Sandal Trees—*Parmelia tinctorum* and *Usnea japonica*

By T. R. Seshadri and S. Sankara Subramanian

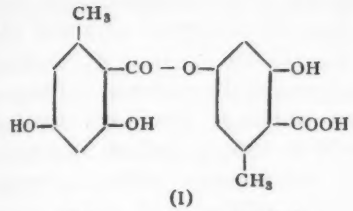
(*From the Departments of Chemistry and Chemical Technology, Andhra University, Waltair*)

Received May 30, 1949

A large number of species of the Parmelia from different parts of the world have been studied by different workers and they seem to differ much in chemical composition. Of the various chemical components of these lichens atranorin, lecanoric, usnic and salazinic acids appear to be the most frequently occurring and a few other acids like stictic, nor-stictic, protocetraric and caperatic are present in certain cases. An Indian lichen, *Parmelia abessinica* growing in the western Andhra districts, was examined by Sastri and Seshadri[1] and found to contain atranorin and lecanoric acid as major components and salazinic acid as a minor component.

The lichen examined now grows on the sandal trees of the Coorg area on the western highlands of South India. The trees do not suffer any adverse effects on account of its growth as contrasted with *Ramalina tayloriana* previously reported.[2] A sample of the lichen was sent to Prof. Y. Asahina of Tokyo and kindly identified by him as *Parmelia tinctorum* Despr. This species is found in all the warmer regions of the world including Japan. Hesse[3] originally examined a sample of this lichen found on the Cinchona bark of the Madras Province and isolated from it atranorin and lecanoric acid. This finding has been confirmed with a Japanese sample (Private communication from Prof. Asahina).

In our study of this lichen a cold ether extract contained, along with some colouring matter of the carotenoid type, lecanoric acid (I) (5·0%) and atranorin (II) (0·8%). A subsequent extraction with hot acetone yielded nor-stictic acid (III) (1·0%). Of these components nor-stictic acid is of rather rare occurrence. It was first isolated by Asahina from *Lobaria pulmonaria*[4] and later from *Parmelia acetabulum*[5] which according to Hesse[6] contained only atranorin and salazinic acid. In our earlier publication on *Parmelia abessinica*[1] attention was drawn to the biogenetic relationship among the three components: lecanoric acid, atronorin and salazinic acid (IV). Nor-stictic acid occurring in *P. tinctorum* is more closely related to atranorin than salazinic acid is. Of these compounds atranorin is found to be definitely toxic to fish whereas lecanoric and nor-stictic acids are nontoxic.



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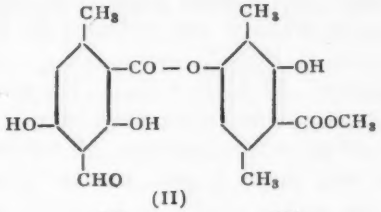

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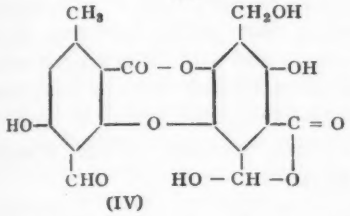

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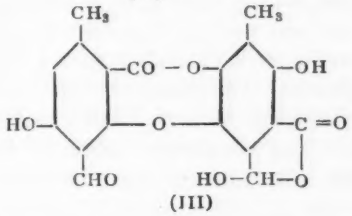
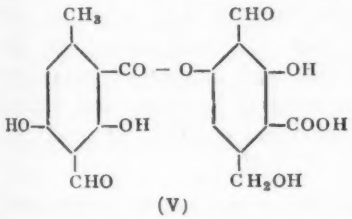


(III)

Along with the predominant growth of *P. tinctorum* a small quantity of a lichen kindly identified by Prof. Y. Asahina as *Usnea japonica* Wain. is also found. This lichen has been hitherto known to occur only in Japan and Formosa. Using the small sample sent for identification, Prof. Asahina could detect the presence of usnic and stictic acids by his micro-chemical method.[7] In his opinion *U. articulata* v. *asperula*[8] which he had found earlier to contain usnic and stictic acids is synonymous with *U. japonica.* In our detailed examination of the Indian sample of *U. japonica* usnic and barbatolic acids (V) could be obtained from the ether extract and stictic acid (VI) from the subsequent acetone extract. The isolation of barbatolic acid from this source is significant since its occurrence along with stictic acid is again of interest from the point of view of biogenesis.[9]



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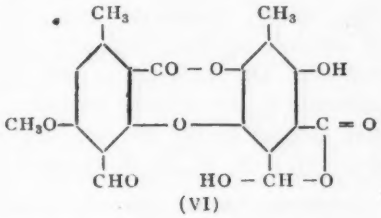

(VI)

EXPERIMENTAL

Parmelia tinctorum

Ether extract (*Atranorin and lecanoric acid*).—500 g. of the powdered lichen was extracted with ether twice by cold maceration (each time lasting for 24 hrs.). The combined ether extract was concentrated to a low bulk when a colourless solid was obtained (Fraction A). This was filtered off,

washed with a small quantity of cold acetone and crystallised twice from benzene when it was obtained in the form of colourless prismatic rods melting at 196–97°; yield, 4·0 g. (Found: C, 60·7; H, 5·2; $C_{19}H_{18}O_8$ requires C, 60·9; H, 4·8%.) The substance was easily soluble in hot benzene and chloroform, moderately in ether and petroleum ether and sparingly in cold alcohol and acetone. It was insoluble in aqueous sodium bicarbonate and only slowly it gave a yellow solution with aqueous sodium carbonate. It was readily soluble in potassium hydroxide solution with a deep yellow colour and with conc. sulphuric acid it gave a deep yellow solution. With alcoholic ferric chloride it gave a wine-red colour and with bleaching powder no colour. The substance was identified as atranorin and this was confirmed by preparing its methyl ether melting at 123–24° by the action of methyl iodide and potassium carbonate in dry acetone medium. Direct comparisons with authentic samples were also made.

The ether mother-liquor left after removing fraction A was evaporated to dryness and the residue treated with hot benzene to remove the small quantities of atranorin still present. The benzene-insoluble solid (fraction B) was taken in cold acetone in which it quickly dissolved and to this solution was added excess of chloroform when a colourless solid separated. This was filtered off and crystallised from acetone-chloroform mixture (1 : 3) when colourless needles melting at 175–76° were obtained; yield, 25·0 g. (Found: C, 60·8; H, 4·3; $C_{16}H_{14}O_7$ requires C, 60·4; H, 4·4%.) The substance was soluble in sodium bicarbonate solution and it gave a red-violet colour with alcoholic ferric chloride and bluish-red with bleaching powder. It was identified as lecanoric acid and the identity was confirmed by fission of the depside link by means of (1) aqueous alkali (5·0%) when orsellinic acid, m.p. 176°, and orcinol were obtained, (2) methyl alcoholic alkali (2·0%) when methyl orsellinate, m.p. 142–43°, and orsellinic acid were got and (3) absolute alcohol when ethyl orsellinate, m.p. 132°, and orcinol were the products. On methylation with methyl iodide and anhydrous potassium carbonate in dry acetone medium, trimethyl ether of lecanoric acid methyl ester melting at 145–46° was obtained as colourless needles. (Found: C, 64·0; H, 6·2; $C_{20}H_{22}O_7$ requires C, 64·1; H, 5·9%.)

Acetone extract (*Nor-stictic acid*).—The lichen residue left after ether extraction was extracted three times with hot acetone (about 6 hrs. each time). The brown solution was distilled to remove the solvent. The residue was boiled with excess of pure chloroform and filtered when a colourless solid was left behind. This was crystallised from hot 80% acetone when colourless needles turning red brown at 260° and melting with decomposition at 285° were obtained; yield, 5 g. (Found: C, 57·6; H, 3·5; $C_{18}H_{12}O_9$ requires C, 58·0; H, 3·2%.) It was very bitter to the taste, insoluble in

chloroform, benzene and water and sparingly soluble in ether, cold acetone and alcohol. In alcoholic solution it gave a wine-red colour with ferric chloride. It dissolved slowly in aqueous sodium bicarbonate giving a yellow colour. When boiled with a concentrated solution of potassium carbonate it formed a red solution from which separated red crystals (in the form of aggregates of long needles) of the potassium salt of nor-stictic acid which could be easily identified by the characteristic crystal appearance under the microscope.[5] Its identity was confirmed by preparing the acetyl derivative melting at 212–13° and the dianil melting at 265° (decomp.).

Toxicity tests.—Using fresh-water fish (*Haplochilus panchax*) as the test animals and following the usual procedure employed in these laboratories,[10] atranorin was found to be toxic in a concentration of 25 mg. per litre in 20 minutes; gelatin in a concentration of 1 g. per litre was used in this experiment to facilitate the solution of the compound in water. Lecanoric and nor-stictic acids were non-toxic even in a concentration of 100 mg. per litre during 24 hours.

Usnea japonica

Ether extract (*d-usnic acid and barbatolic acid*).—The lichen (50 g.) in coarse powder form was extracted in a Soxhlet extractor with ether and the extract concentrated to a small bulk and allowed to stand overnight when a crystalline solid (about 1·4 g.) separated. This was found to be a mixture when examined under the microscope since two different crystalline forms could be seen, yellow prisms and colourless tiny plates. It was digested with petroleum ether (400 c.c.) and filtered. From the petroleum ether filtrate on concentration crystallised yellow prismatic rods melting at 202–03°; yield, 0·8 g. $[\alpha]^{30}$, + 472°. It gave a deep yellow solution with aqueous potassium hydroxide and in alcoholic solution it gave a reddish brown colour with ferric chloride. Mixed melting point with an authentic sample of *d*-usnic acid from *R. tayloriana* was undepressed. The petroleum-ether insoluble residue was washed with hot benzene (20 c.c.). The benzene-insoluble solid was dissolved in sufficient quantity of ether and the ether solution concentrated when a colourless crystalline solid separated in the form of flat needles melting at 204–05° (decomp.) (sintering at 195°); yield, 0·4 g. (Found: C, 55·1; H, 3·7; $C_{18}H_{14}O_{10}$ requires C, 55·4; H, 3·6%.) It was easily soluble in aqueous sodium bicarbonate giving a yellow colour and with aqueous potash gave an intense yellow solution. With alcoholic ferric chloride it gave a deep brown-red colour and no colour with bleaching powder. It was therefore identified as barbatolic acid and this was confirmed by preparing its acetate, m.p. 160–62° (decomp.), by means of acetic anhydride and fused sodium acetate.

Acetone extract (*Stictic acid*).—The residue left after ether extraction was extracted with hot acetone and this extract, on concentration to a low bulk, deposited some colourless crystalline powder. This was filtered off and crystallised twice from anhydrous acetone when a colourless crystalline solid was obtained in the form of aggregates of fine needles. It melted at 265° (decomp.) with sintering and change of colour at 255°; yield, 0·8 g. (Found, C, 59·4; H, 3·4; $C_{19}H_{14}O_9$ requires C, 59·1; H, 3·6%.) It was sparingly soluble in alcohol, acetone and ether and insoluble in benzene and chloroform. It was slowly soluble in aqueous sodium bicarbonate giving a yellow colour and in aqueous potash it gave a bright yellow solution which changed in colour to brown-red on standing without depositing any crystalline salt like salazinic and nor-stictic acids. With alcoholic ferric chloride it gave a violet colour which turned brown with addition of an excess of the reagent. With concentrated sulphuric acid it gave an intense yellow solution which immediately changed to deep red and from this solution separated a reddish brown flocculent precipitate on the addition of a small quantity of water. From these reactions it was identified as stictic acid and this was confirmed by preparing the dianil melting at 232°.

Our thanks are due to Prof. Y. Asahina for kindly identifying the lichens and for his interest in this work.

Summary

Two lichens are found on the sandal trees of Coorg which do not suffer adverse effects on this account. *Parmelia tinctorum* was earlier reported to contain atranorin and lecanoric acid; considerable amounts of nor-stictic acid are now isolated from it. *Usnea japonica* is reported for the first time in India. Besides usnic and stictic acids already known in this source, barbatolic acid also has now been found to be present in it.

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CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part X. Chemical Components of *Teloschistes flavicans*

By T. R. Seshadri and S. Sankara Subramanian

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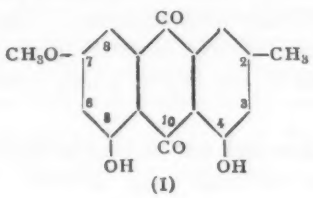
Received May 30, 1949

Along with the luxuriant growth of *Ramalina tayloriana*[1] on the sandal trees of the Simhachalam hills is found a yellow lichen (sometimes markedly orange yellow) in small quantities. Its presence in *R. tayloriana* sample is readily revealed by the isolation from the petroleum-ether extract, besides usnic acid, of a small quantity of an orange coloured substance giving the characteristic colour reactions of polyhydroxy anthraquinones. The lichen is also found on other plants of this area, though in small quantities. A sample of it was sent to Prof. Y. Asahina of Tokyo who kindly identified it as *Teloschistes flavicans* Norm.

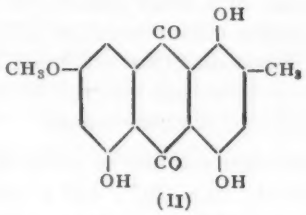
Zopf[2] was the first to study this lichen and was able to isolate from it physcion (I), m.p. 207°, and a colourless substance, m.p. 240–45°. In our experiments with this lichen we first employed ether, acetone and water in succession as solvents. The first solvent removed all crystalline products and the others yielded none. From this ether extract a colourless substance (A) could be readily separated as the alkali-insoluble portion. The alkali-soluble portion gave all the reactions for physcion, but there was difficulty in purifying it. After repeated fractional crystallisation using alcohol-chloroform mixture a fraction melting at 206–207° and agreeing with physcion in every respect could be obtained. But it was clear that a higher melting and a less soluble fraction was present in appreciable quantities and it was the cause of the difficulty in purifying physcion. This difficulty was got over subsequently by employing petroleum ether and chloroform successively for the extraction of the lichen. The petroleum ether extract contained besides the colourless substance (A) almost all the physcion and only minor quantities of the higher melting substance with the result physcion could be readily purified. In the chloroform extract only the higher melting compound was found. It is given the name ' Teloschistin ', since it does not agree with the description of any other naturally occurring compound so far isolated.

Teloschistin crystallises as dull orange plates and thin prisms melting at 229–30° and has the formula $C_{16}H_{12}O_6$ with one methoxyl group. It is

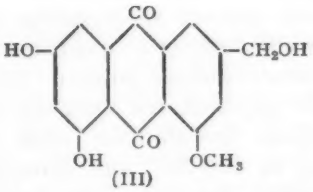
insoluble in sodium bicarbonate and carbonate solutions, but is soluble in cold dilute potassium hydroxide from which red-violet crystals separate on standing. It gives a reddish brown colour with alcoholic ferric chloride and with concentrated sulphuric acid forms a deep orange red solution which in thin layers has an eosin-like shade. In these respects it closely resembles physcion. Its composition would indicate that it has one oxygen atom more than physcion and hence it may be expected to be a hydroxy physcion and this is in accord with its higher melting point and lower solubility in organic solvents. The formation of sparingly soluble potassium salt as well as the insolubility of the substance in aqueous sodium carbonate would indicate the presence of a methoxyl group in the 7-position as in physcion (I) and erythroglaucin[3] (II). Roseopurpurin[4] (III) which has a hydroxyl in the 7-position and a methoxyl in the 4-position is soluble in aqueous sodium carbonate.



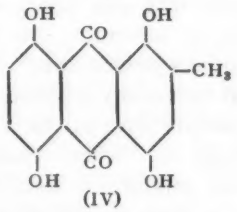
(I)



(II)



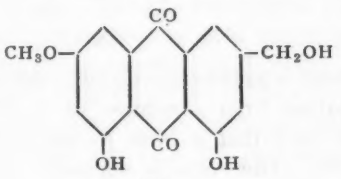
(III)



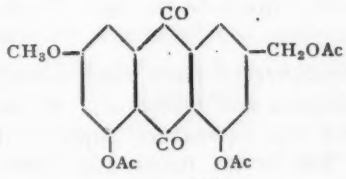
(IV)

The location of the extra hydroxyl group of teloschistin in the physcion structure could be arrived at from the following considerations. Polyhydroxy anthraquinones with hydroxyls para to one another as in 1:4:5 and 1:4:5:8 arrangements exhibit strong fluorescence in glacial acetic acid solution and give a brilliant blue colour with conc. sulphuric acid, *e.g.*, erythroglaucin (II) and cynodontin[5] (IV). But the new compound teloschistin, just like physcion, does not exhibit these characteristics. Hence the presence of the additional hydroxyl in the 1- or 8-position could be ruled out. A close study of the naturally occurring hydroxy anthraquinones would suggest as the next possibility the position in the side chain. Teloschistin would then be ω-hydroxy physcion (V). This constitution is supported by the observation that though it forms a triacetate (VI), m.p.

192–93°, it yields only a dimethyl ether (VII), m.p. 222–23°, one hydroxyl thus remaining unmethylated when methylation is carried out with dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium. Further on treatment with hydriodic acid and red phosphorus in acetic anhydride medium the substance undergoes demethylation and reduction, and the subsequent oxidation of the product with chromic acid yields frangula-emodin (VIII) decomposing at about 255°. This series of reactions would result not only in demethylation but reduction of the ω-hydroxy group also. [Compare conversion of ω-hydroxy emodin (IX) into frangula-emodin (VIII)[6].] The abovementioned structure for teloschistin as ω-hydroxy physcion is thus definitely established.



(V)



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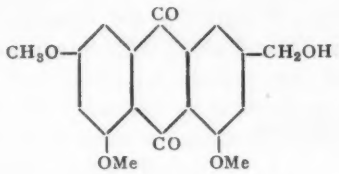
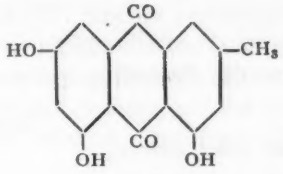
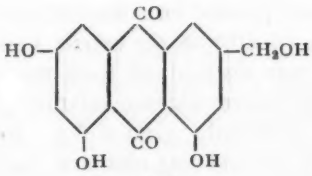


(VII)



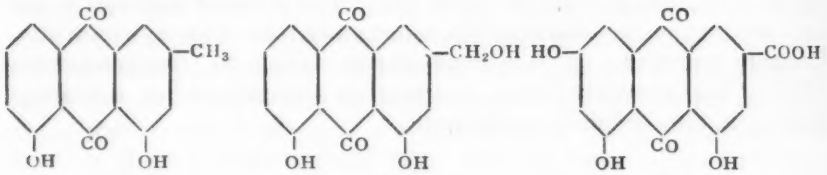
(VIII)



(IX)

In further confirmation of the above conclusion could be mentioned the following:—Raistrick, *et al.*,[6] subjected ω-hydroxy-emodin (IX) to partial methylation and obtained the corresponding 7-monomethyl ether. Its melting point (229–31°) recorded by them agrees with that of teloschistin isolated from *T. flavicans*. Posternak[4] subjected roseopurpurin (III) to energetic methylation and obtained 4:5:7-trimethoxy-2-hydroxymethyl anthraquinone (VII) as a minor product. Its crystal structure and melting point (222–24°) agree with those of the dimethyl derivative of teloschistin.

The association of teloschistin with physcion is rather interesting; the difference is an ω-hydroxyl group. Similar pairs are found in chrysophanol (X) and aloe-emodin (XI) occurring in *Cascara sagrada*.[7] A different type of association involving an additional nuclear hydroxyl is found in a number of *Aspergillus glaucus* species[3] which contain physcion (I) and erythroglaucin (II).



(X) (XI) (XII)

Physcion (I) is fairly widely distributed in lichens especially in the species of Xanthoria and Placodium. Its isolation from a number of moulds by Raistrick and co-workers[3] supports the view that it owes its origin to the fungal half of the fungus-alga symbiont. This view is supported further by the present isolation of teloschistin from *T. flavicans*, because the closely related ω-hydroxy emodin (IX) having a hydroxyl in the 7-position instead of the methoxyl of teloschistin has been found along with emodic acid (XII) in the mould, *Penicillum cyclopium*.[6]

Experimental

Petroleum ether extract

[*Physcion* (*I*), *Teloschistin* (*V*) *and colourless substance A*].—250 g. of the air-dried lichen in coarse powder form was extracted in a Soxhlet extractor with light petroleum (b.p. 60–80°) till the extract syphoning over was almost colourless. The solvent was distilled off from the extract and the residue was crystallised from chloroform–alcohol mixture (1 : 1) when fraction I melting above 215° was collected; yield 0·3 g. From the mother-liquor after addition of excess of alcohol was obtained fraction II melting at 190–95°; yield, 2·1 g.

Fraction I [*Teloschistin* (*V*)].—Fraction I was recrystallised twice from hot benzene when it was obtained in the form of dull orange rectangular plates and thin prisms melting at 229–30°; yield, 0·2 g. (Found: C, 64·2; H, 4·0; OCH_3, 10·6; $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0; and OCH_3, 10·3%.) It was sparingly soluble in petroleum ether, alcohol and acetone, moderately in benzene and more easily in hot chloroform and glacial acetic acid. It was not soluble in aqueous sodium bicarbonate and carbonate, but soluble in 2N potassium hydroxide giving a deep purple red solution

from which separated red-violet crystals after standing for some time. With conc. sulphuric acid it gave a deep orange red solution which in thin layers had an eosin-like shade. With alcoholic ferric chloride it gave a reddish-brown colour. It did not exhibit fluorescence in glacial acetic acid solution.

Fraction II [*Physcion* (*I*), *and colourless substance A*].—Fraction II was treated with sodium hydroxide solution (5%) and immediately filtered. The residue (R) was washed with plenty of water and the filtrate and washings were acidified when an orange coloured crystalline substance separated. This was filtered off, washed with water till free from acid and twice recrystallised from alcohol-chloroform mixture when it came out as long reddish-orange needles melting at 206–07°; yield, 1·6 g. (Found: C, 67·3; H, 4·5; OCH_3, 11·3; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2 and OCH_3, 10·9%.) It was sparingly soluble in cold petroleum ether, methanol and acetone but quite soluble in benzene, chloroform and glacial acetic acid. Its solubility in all the solvents was more than in the case of teloschistin. It gave a beautiful magenta colour in dilute solution with conc. sulphuric acid and a rose-pink solution with 2N potassium hydroxide from which a rose-pink precipitate slowly separated. With alcoholic ferric chloride it gave a reddish brown colour. From these it was identified as physcion and this was confirmed by preparing the diacetyl derivative melting at 186–87°.

The alkali-insoluble residue (R), after washing with plenty of water, was dried and dissolved in chloroform-methanol mixture and the solution allowed to stand when a colourless crystalline solid (A), melting at 245–50°, was obtained; yield, 0·2 g.

Chloroform extract

[*Teloschistin* (*V*)].—The lichen powder left after extraction with petroleum ether was extracted in the same apparatus with chloroform and the extract on evaporation left a dull orange coloured solid melting above 200°. It was first crystallised from alcohol-chloroform mixture and the product melting above 220° was recrystallised twice from hot benzene when dull orange-coloured rectangular plates and thin prisms melting at 229-30° were obtained; yield, 1·3 g. Mixed melting point with the product obtained from fraction I was undepressed. The colour reactions were identical.

Triacetate (*VI*).—Teloschistin (0·3 g.) was dissolved in acetic anhydride (15 c.c.) and boiled for ten minutes under reflux with a few drops of conc. sulphuric acid. The greenish yellow solid that separated when the solution was poured into water, was crystallised from glacial acetic acid when lemon yellow large rectangular plates melting at 192–93° were obtained. The

product did not give any colour with alcoholic ferric chloride. (Found: C, 61·8; H, 4·0; $C_{22}H_{18}O_9$ requires C, 61·9 and H, 4·3%.)

Dimethyl ether (*VII*).—The substance (0·4 g.) was dissolved in dry acetone (150 c.c.) and dimethyl sulphate (0·8 c.c.) and anhydrous potassium carbonate (10 g.) were added. The mixture was refluxed for 20 hours, the solvent was evaporated and the residue treated with a little water. The yellow solid that separated was crystallised from a large volume of alcohol when it was obtained as fine long yellow needles melting at 222–23°; yield, 0·3 g. It did not give any colour with alcoholic ferric chloride. (Found C, 66·3; H, 4·6; $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·8%.) Posternak[4] reported the melting point of 4: 5: 7-trimethoxy-2-(hydroxy-methyl) anthraquinone as 222–24°.

Demethylation and reduction to frangula-emodin [(4: 5: 7-*trihydroxy 2-methyl-anthraquinone* (*VIII*)].—A mixture of teloschistin (0·5 g.), acetic anhydride (10 c.c.), hydriodic acid (3 c.c., sp. gr. 1·7) and red phosphorus (0·6 g.) was boiled under gentle reflux for three hours. The reaction mixture was cooled and poured into water. The pale brown solid that separated was filtered off, washed and dried. The dry solid was extracted with boiling glacial acetic acid (40 c.c.) and the solution allowed to cool overnight when a granular pale brown powder was obtained which appeared as almost colourless tiny plates under the microscope. When heated it began to darken at 250° and finally decomposed. (Decomposition point of 4: 5: 7-trihydroxy-2-methyl anthranol, 250–58°[6].)

The anthranol (0·3 g.) was dissolved in boiling glacial acetic acid (40 c.c.) and chromium trioxide (0·5 g.), dissolved in acetic acid (10 c.c. glacial acetic acid and 2 c.c. water), was added quickly. The mixture was kept at 60° (water-bath) for 30 minutes and then poured into water (250 c.c.). It was ether-extracted and the ether extract washed with water till free from acid and the residue (0·2 g.) left after evaporation of the ether was crystallised from glacial acetic acid when orange yellow needles melting at 250–55° (decomp.) separated. The product was identified as frangula-emodin (VIII) by means of its colour reactions and analysis. (Found: C, 66·5; H, 4·0; $C_{15}H_{10}O_5$ requires C, 66·7 and H, 3·7%.)

Our thanks are due to Prof. Y. Asahina for the identification of the lichen.

Summary

A yellow lichen accompanying *Ramalina tayloriana* has been identified as *Teloschistes flavicans*. Besides physcion and a colourless substance, another orange coloured compound melting at 229–30° and having the

formula $C_{16}H_{12}O_6$ is now isolated. It is designated 'Teloschistin'. It resembles physcion closely and its constitution is established as 4:5-dihydroxy-7-methoxy-2-hydroxymethyl anthraquinone (ω-hydroxy physcion).

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2. Zopf .. *Ann.*, 1905, **340**, 300.
3. Ashley, *et al.* .. *Biochem. J.*, 1939, **33**, 1291.
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6. Anslow, *et al.* .. *Ibid.*, 1940, **34**, 159.
7. Lidder, *et al.* .. *J. Amer. Pharm. Ass.*, 1942, **31**, 1616.

A NEW OCCURRENCE OF MAHADEVITE

By E. Venkayya, M.Sc.

Received May 16, 1949
(Communicated by Prof. C. Mahadevan, D.Sc., F.A.Sc.)

Samples of books of mica resembling the new type of mica described by Ramaseshan (1945) in physical appearance were sent by Messrs. Krishna Crucible Company of Mamidada to Prof. Mahadevan for investigation and report. This paper embodies the results of the physical, optical and chemical properties of the mica carried out by the author in the Geology Department of the Andhra University.

In hand specimens the mica appears opaque in thick sheets, transparent in thin laminæ, fresh looking with a bright bronze colour and lustre and does not show any alteration or leaching of colour. It is characterised by a perfect basal cleavage, yielding thin, elastic and flexible laminæ with a feeble yellow tinge. When struck with a blunt pointed knife it gives like other micas a six rayed percussion figure. From the position of the longer and more prominent ray of the percussion figure, the plane of the optic axes is found to be perpendicular to the clino-pinacoid, and shows affinity to muscovite group. The interference figure approximates to that of an uniaxial figure with a small optic axial angle. However, from the central points of the two isogyre brushes in the 45° position, the apparent optic axial angle in air for the specimen is determined by the formula,

$$D = K \sin E.$$

where

D = Half the distance between two melatopes $= 1 \cdot 5\, d$.

E = Half the apparent optic axial angle in air.

K (Constant of the microscope) $= 6 \cdot 000$.

The pleochroic scheme of the mineral is

Z = Y = Yellowish brown.

X = Golden yellow.

The average optic axial angle is 14°, optically negative with the X-direction very nearly coinciding with the normal to (001) or slightly makes an angle of 1° to 2° as in the case of biotite. The mean refractive index β for the specimen has been determined for a number of flawless pieces devoid

of air films and interference colours by immersion in index liquids. The β refractive index amounts to $1 \cdot 586 \pm 0 \cdot 002$.

Analytical data

In the analytical Table I, column (1) shows the analysis of mica sent by Krishna Crucible Company and (2), the analysis of Mahadevite from the collection of Prof. Mahadevan. Columns (3) and (4) are the analyses of Mahadevite carried out by Ramaseshan (1945) and quoted from his paper for comparison.

TABLE I

	1	2	3	4
SiO_2 ..	36·51	35·42	38·98	38·24
Al_2O_3 ..	27·38	28·28	29·94	29·20
Fe_2O_3 ..	2·78	2·81	4·12	3·86
FeO ..	1·77	1·92		
MgO ..	17·21	16·36	13·20	14·40
CaO ..	·53	·74	·40	·50
K_2O + Na_2O ..	9·98	10·94	9·60	9·20
TiO_2 ..	..	..	..	..
H_2O ..	3·80	3·72	3·80	3·80
	99·96	100·19	100·13	99·20

(1) Mica—Krishna Crucible Company, Analyst : E. Venkayya.

(2) Mahadevite—Racha Konda, Bison Hill Range, Analyst : E. Venkayya.

(3) and (4) Mahadevite— *Proceedings of the Indian Academy of Sciences*, **22**, Sec. A, pp. 179, (1945), Analyst : S. Ramaseshan.

The similarity in the optical characters of the new mica is supported by the analytical data which does not disclose any wide differences in the amounts of the various constituents when compared with Mahadevite. As in the case of Mahadevite, the specimen shows a higher content of magnesia than in muscovite; a lower percentage amount of iron than in biotite and too much alumina to be phlogopite. It is quite evident both from the optical and chemical studies that the specimen sent by Krishna Crucible Company is a new occurence of Mahadevite mica found associated with the pegmatites in the khondalitic region of the East Godavari District.

In column (1) of Table II, the average composition of Mahadevite is given in weight percentages of the various constituents of the four available analyses except for iron. The average amounts of ferric and ferrous iron are determined from the analyses 1 and 2 since Ramaseshan (1945) has given only the total iron oxides in his analyses. Columns (2) and (3) show the

molecular proportions, and numbers of different molecules in the mica respectively.

TABLE II

	1 Wt. Perc.		2 Mol. Prop.	3 No. Mols.
SiO_2 ..	37·29	0·621	0·621	5·5
Al_2O_3 ..	29·20	0·286	0·303	3
Fe_2O_3 ..	2·79	0·017		
FeO ..	1·85	0·025	0·394	3·5
MgO ..	14·79	0·369		
CaO ..	·56	0·009	0·114	1
K_2O ..	9·93	0·105		
Na_2O ..				
TiO_2 ..	..	..	..	..
H_2O ..	3·78	0·206	0·206	2
	100·19			

The molecular proportion of ferrous iron is added to that of magnesium and ferric iron to alumina since ferrous and ferric iron can proxy for magnesium and aluminium respectively in micas. The low amount of CaO is combined with the alkalies. Assuming the number of alkali molecules as 1, the relative number of molecules of the other constituents are calculated and represented in column (3). From this, the formula for Mahadevite is computed as follows, and compared with the formulæ of muscovite and phlogopite.

Mahadevite	$2(H_2K)O$	$3·5(MgFe)O$	$3(Al_2O_3)$	$5·5\ SiO_2$
Muscovite	$2(H_2K)O$		$3(Al_2O_3)$	$6\ SiO_2$
Phlogopite	$2(H_2K)O$	$6\ MgO$	Al_2O_3	$6\ SiO_2$

Muscovite and phlogopite are type representatives of the heptaphyllite and octophyllite micas respectively. The two groups of micas though crystallising in the same system do not show complete miscibility in all proportions. In the former group the ratio between Al and Si is 1 : 2 while in the latter kind the proportion is 1 : 6. The absence of magnesium in muscovite and the deficiency of alumina in phlogopite are well brought out in the above formulæ of Winchell (1945). But comparative study of the chemical composition and the computed formula of Mahadevite with the above two micas shows that both alumina and magnesia are present in it in equal proportions, giving to it an intermediate position between muscovite and phlogopite. The existence of equal proportions of alumina and magnesia have not so far been recorded and in such a case Mahadevite may be considered as one where magnesium and aluminium exist in equal proportions. It is presumed

that Mahadevite with its equal proportions of Al and Mg may be conceived as a link between muscovite and phlogopite.

These investigations go to show that the new type of mica reported by Ramaseshan is a distinct species in the mica group and is not due to the alteration of any of the known micas.

Summary

Samples of mica similar to Mahadevite sent by Messrs. Krishna Crucible Company of Mamidada from the East Godavari District, were studied optically and were chemically analysed. The percussion figure indicates its affinity to the muscovite group. The mica is optically negative, the apparent optic axial angle being about 14°. The molecular formula has been calculated from the analysis and it is shown that this mica has an intermediate position between muscovite and phlogopite. Ramasehan's observation that this mica is a distinct species and not an alteration product of any other mica is confirmed.

The work was carried out in the Research Laboratories of Andhra University. The author wishes to express his grateful thanks to Prof. C. Mahadevan for the supply of material and guidance throughout the work.

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXII. A Synthesis of Pectolinarigenin

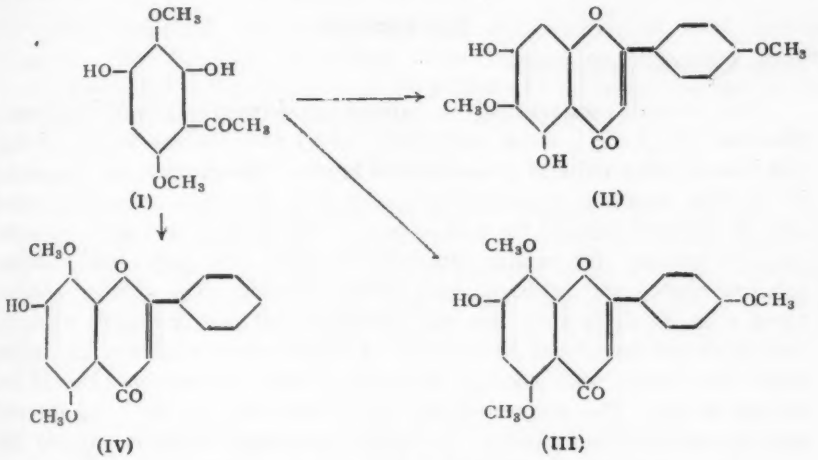
By V. V. Sreerama Murti and T. R. Seshadri
(From the Department of Chemistry, Andhra University, Waltair)

Received May 30, 1949

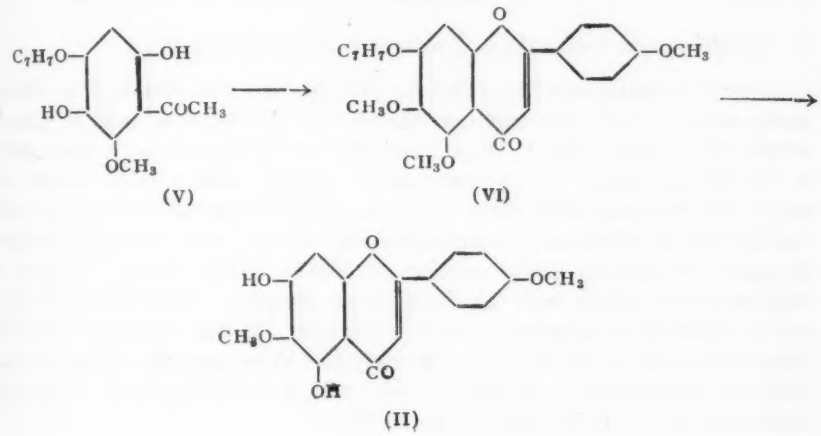
The glycoside pectolinarin which was isolated from the flowers of *Linaria vulgaris*[1] yielded on hydrolysis an aglycone, pectolinarigenin, having the molecular formula $C_{17}H_{14}O_6$. It was a dimethyl ether of scutellarein. The position of one of the methoxyl groups could be easily located since it yielded anisic acid by alkali fission. The other methoxyl was considered to be in the 6-position since the compound was found to be identical with the 6: 4′-dimethyl ether of scutellarein (II) obtained synthetically by Wessely and Moser.[2] The sugar residue could be allotted the position 7 because the glycoside was unchanged when treated with diazomethane and hence had the free hydroxyl group in the resistant 5-position. Subsequently the synthesis of the glycoside itself has been effected using the aglycone and hexa-acetyl-β-rutinosidyl bromide.[3]

The synthesis of pectolinarigenin by Wessely and Moser[2] was not a direct one and was due to the Allan-Robinson condensation taking an unexpected course. They fused 2: 4-dihydroxy-3: 6-dimethoxy acetophenone (I) with anisic anhydride and sodium anisate and instead of the expected 7-hydroxy-5: 8: 4′-trimethoxy flavone (III), obtained a dimethyl ether of scutellarein (II). This was explained as due to partial demethylation during the condensation and favoured ring closure to yield the 5: 6: 7-arrangement instead of the 5: 7: 8-arrangement of groups.

However, attempts to synthesise oroxylin–A by employing the same ketone and benzoic anhydride and sodium benzoate were unsuccessful.[4] Only wogonin methyl ether (IV) was obtained. Even in anisoylation Wessely and Moser got the normal product (III) in one of a large number of experiments and Furukawa and Tamaki[5] reported that the condensation proceeded normally in their experiments to yield 5: 8: 4′-trimethoxy-7-hydroxy flavone (III). Hence a more definite synthetic route for scutellarein -6: 4′-dimethyl-ether was needed and this has now been provided by the synthesis of the



compound on the same lines as oroxylin-A.[6] By fusing 2: 5-dihydroxy-4-benzyloxy-6-methoxy acetophenone (V) with sodium anisate and anisic anhydride and methylating the product, is obtained 5: 6: 4′-trimethoxy-7-benzyloxy flavone (VI). It undergoes debenzylation and partial demethylation in the 5-position with hydrobromic acid and the product is a dimethyl ether having all the properties of pectolinarigenin (II). Its diacetate also agrees with the description of pectolinarigenin diacetate. We have also repeated the synthesis by the method of Wessely and Moser[2] and find that the product is identical with the one obtained by the new method, the same being the case with the diacetate obtained from it.



Experimental

Allan-Robinson condensation

An intimate mixture of 2: 5-dihydroxy-4-benzyloxy-6-methoxy-acetophenone (V) (2·5 g.), anisic anhydride (16 g.) and sodium anisate (6·0 g.) was heated under reduced pressure for 4 hours. The product was suspended in alcohol, aqueous potassium hydroxide (8 g. in 10 c.c. of water) added and the mixture refluxed for half-an-hour. The alcohol was removed under reduced pressure, the residue dissolved in water, the deep reddish-brown solution filtered and saturated with carbon dioxide. The alkaline solution along with the fluffy solid that had separated out was repeatedly extracted with ether and the solvent distilled off. A bright yellow solid was left behind which was boiled with aqueous alcoholic sodium carbonate (5%, 25 c.c.) for two hours. The yellow solution was filtered and acidified and the product crystallised from alcohol. It melted indefinitely between 210 and 230° and gave a green ferric chloride colour (yield, 0·7 g.). It was, therefore, considered to be a mixture of 5-methoxy and 5-hydroxy compounds and hence was directly subjected to methylation.

5: 6: 4′-*Trimethoxy-7-benzyloxy-flavone* (*VI*)

The yellow solid obtained above (0·5 g.) was dissolved in dry acetone (50 c.c.), redistilled dimethyl sulphate (0·8 c.c.) and ignited potassium carbonate (5 g.) were added and the mixture refluxed for 30 hours. The product could be crystallised from acetone-alcohol mixture when it was obtained as colourless rods and prisms melting at 184–5°; yield, 0·4 g. (Found: C, 71·6; H, 5·5; $C_{25}H_{22}O_6$ requires C, 71·8; H, 5·3%.)

5: 7-*Dihydroxy*-6: 4′-*dimethoxy flavone*: *Pectolinarigenin* (*II*)

The trimethoxy-benzyloxy flavone (VI) (0·5 g.) was dissolved in glacial acetic acid (15 c.c.), the solution treated with hydrobromic acid in glacial acetic acid solution (40%; 10 c.c.) and the mixture heated on a water-bath at 60° for one hour. It was then cooled, diluted with a large volume of water and extracted with ether. On removing the solvent, a yellow solid was left behind which, on crystallisation from alcohol, was obtained as yellow elongated rectangular plates melting at 216–7°. Yield, 0·1 g. It gave a reddish-brown colour with alcoholic ferric chloride, and dissolved to a yellow solution in aqueous sodium hydroxide. It was identical with the sample obtained by the method of Wessely and Moser and the mixed melting point was undepressed. (Found: C, 64·7; H, 4·7; OCH_3, 19·9; $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5 and OCH_3 19·7%.)

The compound was acetylated with acetic anhydride and sodium acetate. The diacetate crystallised from alcohol as colourless needles melting at 152–3°; the mixture with the acetate of the sample obtained by the method of Wessely and Moser melted at same temperature.

Summary

Employing 2: 5-dihydroxy-4-benzyloxy-6-methoxy acetophenone and following the procedure very similar to the one adopted for the synthesis of oroxylin-A, the 6: 4′-dimethyl ether of scutellarein has now been obtained. Its properties agree closely with those of pectolinarigenin and it is found to be identical with the dimethyl ether prepared by the method of Wessely and Moser.

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DIELECTRIC CONSTANTS OF CRYSTALS—III

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1. Introduction

There are discrepancies in the dielectric constants of some crystals in different directions reported by previous investigators. An accurate knowledge of the directional dependence of dielectric constant is required for an understanding of the relation between dielectric behaviour and crystal structure. So the author has undertaken a determination of the dielectric constants of a number of crystals and the results in some of them are reported in this paper.

2. Experimental

Barium nitrate, Lead nitrate and Sodium chlorate.—Plates are cut from transparent, solution grown crystals of the above. As these are cubic crystals, any orientation will give the same constant and so, the plane which gives the largest area is chosen for cutting.

Rocksalt and Fluorite.—Sections are cut from clear transparent minerals. Another two sections of fluorite, one from a green-coloured crystal and one from a pale-blue coloured crystal are also cut.

Spinel.—A plate is taken for investigation from a perfectly transparent, artificially grown lump.

Calcite, Apatite and Citrine.—Sections from flawless, transparent varieties of calcite, apatite and citrine, parallel and perpendicular to the optic axis of each, are cut. Citrine is light yellow in colour.

Zircon.—An opaque brownish crystal with well-developed faces is used for taking sections.

Beryl.—Specimen I is colourless and specimen II is of green colour. These are not quite transparent, but somewhat cloudy.

Corundum.—Three different specimens are used. All are opaque. Specimen I is chocolate coloured, specimen II is of brown colour with uniform

texture and specimen III is of slate colour with specks of foreign material embedded here and there.

Tourmaline.—Different specimens are used. Specimen I is translucent and light yellow in colour. Some portion of it is green. Specimen 2 is rose red in colour, and transparent. In thin sections, it is almost colourless. Specimen 3 is black in bulk, but dark green and transparent in very thin sections. Specimens 4, 5, 6, 7, 8, are all black in colour. All the crystals have well-developed faces.

Sulphur and Barites.—These are orthorhombic crystals and sections $\perp^r$ to the three crystallographic axes *a*, *b*, *c* are required. The three sections are obtained from three small, solution grown crystals of sulphur, which are clear and transparent. Barites, used for taking the sections, is a perfectly transparent and colourless mineral.

The dielectric constants for all the above sections are determined by a liquid mixture method, in which air film errors are avoided. The details of the method can be known from an earlier communication by the author.[1] The values are determined at a frequency of 1·6 megacycles/sec.

3. Results

The dielectric constants of crystals belonging to the cubic system are given in Table I and those of uniaxial crystals in Table II. The dielectric constants of the two orthorhombic crystals are given in Table III.

Table I

Crystal	Dielectric constant	
	Author	Previous values
Barium nitrate ..	5·7	5·2[2], 4·95[3] (for powder)
Lead nitrate ..	16·0	14·8[2], 16[4], 16·8[5] (for powder)
Rock-salt ..	5·8	6·29[6], 5·60[4], 6·2[8], 5·62[5], 6·36[9], 5·6[3]
Sodium chlorate ..	5·9	5·8[10],
Fluorite Sp. I ..	6·9	6·92[6], 6·70[4], 6·85[8]
Fluorite Sp. II ..	6·95	
Fluorite Sp. III ..	7·0	
Spinel ..	8·6	

TABLE II

Crystal	Density	Dielectric constant			
		Author		Other investigators	
		$\parallel^{ly}$	$\perp^{r}$	$\parallel^{ly}$	$\perp^{r}$
Calcite ..	..	8·20	8·70	7·56[11], 8·29[12], 8·0[4] 11[7]	8·49, 8·78, 8·5, 10·1
Beryl Sp. I ..	..	6·8	7·6	7·44[6], 6·05[8], 5·52	7·85, 7·10, 6·05
Beryl Sp. II ..	..	6·9	7·5	5·8[7], 6·07[13]	6·0, 7·02
Apatite ..	..	8·6	10·2	7·4[4], 7·7[7]	9·5, 10·5
Corundum Sp. 1 ..	3·82	10·9	9·6		
Corundum Sp. II ..	3·85	10·9	9·5	11·42[13]	13·17
Corundum Sp. III ..	3·88	11·3	9·8		
Zircon ..	..	12·85	12·6	12·6[4], 8·7[7]	12·8, 8·4
Citrine ..	..	4·70	4·55		
Tourmaline Sp. 1 ..	3·06	6·5	7·9	6·3[8], 5·6[4], 6·5[13]	7·1, 6·7, 7·1
,, (Red) Sp. 2 ..	3·05	6·0	7·4	6·1[7]	7·1
,, (Green) Sp. 3 ..	3·16	5·9	6·8		
,, (Black) Sp. 4 ..	3·18	6·4	8·0		
,, (Black) Sp. 5 ..	3·14	6·3	7·9		
,, (Black) Sp. 6 ..	3·11	6·1	7·6		
,, (Black) Sp. 7 ..	3·11	5·9	7·5		
,, (Black) Sp. 8 ..	3·09	5·8	..		

TABLE III

Crystal	Investigator	ϵ_a	ϵ_b	ϵ_c
Sulphur ..	Author	3·60	3·90	4·60
	Schmidt[4]	3·62	3·85	4·66
	Liebisch and Rubens[7]	3·81	3·97	4·77
	n^2_∞	3·53	3·79	4·48
Barites ..	Author	8·1	13·2	8·2
	Schmidt[4]	7·65	12·2	7·7
	Fellinger[11]	7·0	11·0	7·0
	Errera and Brasseur[2]	7·65	12·6	7·7

4. DISCUSSION OF RESULTS

The previous values reported for barium nitrate and lead nitrate were determined in the powder form. The present values are determined with plates cut out of solution-grown crystals. The dielectric constant of barium nitrate is found to be considerably higher than any of the previously reported values. There is very good agreement among the different values reported for colourless, clear fluorite. The value for the green-coloured type is slightly higher. The results for rock-salt, one of the crystals studied by a

large number of investigators, are however somewhat discordant. The slight hygroscopic nature of the crystal may be the reason to some extent, as any slight moisture on the plate will give a raised value. The most probable value for the dielectric constant of sodium chloride appears to be 5·7.

The first four crystals in Table II, namely calcite, beryl, apatite and corundum, are optically negative. The refractive index is greater when the electric vector is $\perp^r$ to the optic axis than when it is $\|^{ll}$ to it. The dielectric constant also varies with direction in a similar way. For corundum, however, the dielectric constant as determined in this investigation, is larger in the direction of the smaller refractive index. Magnesite, which is also optically negative, is reported[2] previously to have exhibited a greater dielectric constant in the $\|^{ll}$ direction. In this respect of having a higher dielectric constant in the direction of lower refractive index, these two crystals are behaving similarly.

The dielectric constants of corundum determined by the author do not agree with those reported by Fellinger. But the author's values are repeated with different specimens and in each case $\epsilon_{\|} > \epsilon_{\perp}$. The average density of specimen III is more than that of specimen I or of specimen II, and unlike the other two, that specimen is having some inclusions of foreign material here and there. These may be the reasons for its higher values.

Zircon and citrine are optically positive crystals. Accordingly, the dielectric constants of these crystals are smaller in the $\perp^r$ direction than those in the $\|^{ll}$ direction. Schmidt's values for zircon with $\epsilon_{\|} > \epsilon_{\perp}$ do not agree with the author's values. Though the dielectric constants of amethyst were found much higher than those of colourless quartz, the constants of citrine are very nearly the same as those of ordinary quartz.

Tourmaline is an optically negative crystal and accordingly the dielectric constant in the $\perp^r$ direction is greater than that in the $\|^{ll}$ direction for all the specimens examined. But the values differ much from specimen to specimen, the $\perp^r$ value varying between 6·8 and 8·0 and the $\|^{ll}$ value between 5·8 and 6·5. For those specimens, which have a dielectric constant of 6·3 to 6·5 parallel to the axis, the perpendicular constant is also high and is of the order of 7·8 to 8·0. There does not seem to be any correspondence between density and dielectric constant for the different specimens examined. The differences may be due to the different chemical constitutions and impurities. Tourmaline is a complex silicate of boron and aluminium with also either magnesium, iron or an alkali metal present, giving rise to three different types known as magnesium tourmaline, iron tourmaline and alkali tourmaline. The specimens examined, exhibiting different colours, may belong to these different classes. When the black specimens, which probably belong

to the iron class, are alone considered, the dielectric constants seem to vary regularly with density, decreasing with lower density.

For sulphur $n_a < n_b < n_c$ and the dielectric constants also vary in the same way. Values of n_∞ in each of the three directions are calculated, using Cauchy's dispersion formula from the data given in Landolt and Bornstein's Tables for the refractive indices in the visible region and values of n^2_∞ are given in Table III. The agreement between n^2_∞ and ϵ in every direction is striking. Addenbroke[14] has previously drawn attention to the fact that n_∞^2 and ϵ are almost equal in the case of all non-metallic elements.

Barites has $n_a > n_b > n_c$, whereas the dielectric constants do not vary in a similar way. The constant along the b axis is the highest. For strontium sulphate[4] also ϵ_b is the highest whereas n_b is intermediate. In this respect, the behaviour is analogous to the magnetic case. Krishnan, Guha and Banerjee[15] reported that $\chi_b > \chi_c > \chi_a$ for these two crystals.

5. Summary

The dielectric constants of fifteen crystals belonging to different systems are determined and reported together with previous values. Some of the values are found to be different from those reported by earlier investigators. Different specimens of tourmaline are found to have widely different dielectric constants. As against previous report, corundum is found to have a higher dielectric constant in the direction of smaller refractive index.

The author wishes to express his grateful thanks to Prof. S. Bhagavantam under whose guidance the above investigation has been carried out.

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STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION

Part XXXIII. The Rotatory Dispersion of the Enantiomorphic Forms of *p*-Aminobenzene sulphonylamido-2-thiazolecamphor-β-sulphonate, *p*-Sulphonamidophenyliminocamphor, Camphor-β-sulphonylchloride, Camphor-β-sulphonyl-α-pyridylamide and Camphor-β-sulphonyl-α-thiazoleamide

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In a previous communication,[1] the camphor-β-sulphonates (*d*-, *l*- and *dl*-) of some heterocyclic bases were studied. In the present paper we have extended our work to the optically active and racemic forms of *p*-amino benzenesulphonamido-2-thiazolecamphor-β-sulphonate, *p*-sulphonamido-phenyliminocamphor, camphor-β-sulphonylchloride, camphor-β-sulphonyl-α-pyridylamide and camphor-β-sulphonyl-α-thiazoleamide.

Influence of Wavelength on Rotatory Dispersion

The rotatory dispersion of all the optically active substances described in this paper has been determined in the visible region of the spectrum for 12 wavelengths from λ_{6708} Å.U. to λ_{4358} Å.U. (Tables III to VII). It is found to be " simple " as it can be expressed by the one-term Drude's equation, $[\alpha]=\frac{k_0}{\lambda^2-\lambda^2}$. In this equation, k_0 is a constant which is independent of the effects of dispersion. It may be considered as a measure of the absolute rotatory power of the substance. It refers to that wavelength λ, where $\lambda^2-\lambda_0{}^2=1$ square micron, a value of λ not very much greater than 10,000 Å.U. Since measurements recorded in the present investigation are upto 6708 Å.U., an extrapolation, when the dispersion is simple, to a value of λ slightly greater than 10,000 Å.U., is both simple and accurate. In such cases, k_0 may be termed the " Absolute " rotation of the compound.

The Physical Identity of Enantiomers

The rotatory power of *d*- and *l*- enantiomers (Tables III to VII) are identical within the limits of experimental error and thus support Pasteur's

law of Molecular Dissymmetry according to which the optically active and opposite isomers possess rotatory powers identical in magnitude but opposite in sign. In the case of all the compounds described in this paper, the calculated values of rotatory power (c) for different wavelengths agree with the observed ones (o). The calculated values (c) and the differences ($o-c$) are omitted from the Tables (III to VII) for the sake of economy of space. Out of 526 observations recorded, in as many as 468 cases, the differences between the observed and the calculated values of specific rotations correspond to a deviation of 0·02° or less in the observed angle of rotation, and in as many as 37 cases this deviation lies between 0·02° and 0·03°. Only in 23 cases, mostly for Hg_{4358} and Cd_{6439} (mercury violet and cadmium red)—lines difficult to read—this difference lies between 0·03° and 0·05°. These deviations between the observed and the calculated values of rotatory power are, however, of the nature of casual experimental errors.

Nature of the Racemic Modifications

The melting points of the racemic modifications of *p*-aminobenzenesulphonylamido-2-thiazole camphor-β-sulphonate, *p*-sulphonylamidophenyliminocamphor, camphor-β-sulphonylchloride and camphor-β-sulphonyl-α-pyridylamide are higher than those of their optical isomers. They are, therefore, true *dl*- compounds in the solid state. The melting point of the racemic form of camphor-β-sulphonyl-α-thiazole amide is identical with that of its optical isomer. That the racemic form of this substance is also a true *dl*-compound was determined in the following way: a small amount of the *d*-form was added to the corresponding racemic modification and the melting point of the mixture was lowered showing thereby that the racemic modification is a true *dl*- compound.

The Molecular Rotatory Dispersion of Camphor-β-Sulphonates in Aqueous Solution and Comparison of the Value of $[M]_D^{35°}$ of Camphor-β-Sulphonate ion In Water

The values of $[M]_\lambda^{35°}$ in aqueous solution for *p*-aminobenzene sulphonylamido-2-thiazole-*d*-camphor-β-sulphonate are given in Table I. Its value of $[M]_D^{35°}$ is found to be $+65·73°$. As this value of the rotatory power of the salt is higher than the mean value of $[M]_D^{35°}$ of the camphor-β-sulphonate ion (53–54°)[2] and as the observed molecular rotatory power of the salt in aqueous solution is the sum of the rotatory powers of the active acid ion and the non-ionised molecule, it is clear that the undissociated molecule has higher rotatory power and that the salt is not completely electrolytically dissociated even in 0·5% aqueous solution.

TABLE I

Line	$[M]_{\lambda}^{35°}$ in aqueous solution for camphor-β-sulphonates of *p*-aminobenzene-sulphonamido-2-thiazole (0·5000 gm./100 c.c.)
Hg_{4358} ..	265·1°
Li_{4603} ..	180·2
Cd_{4678} ..	168·0
Cd_{4800} ..	155·8
Cd_{5086} ..	119·6
Ag_{5209} ..	107·1
Hg_{5461} ..	87·76
Hg_{5780} ..	68·17
Na_{5893} ..	65·73
Li_{6104} ..	60·87
Cd_{6438}	58·43
Li_{6708} ..	38·95

THE EFFECT OF SOLVENT ON THE ROTATORY POWER

The molecular rotatory power, $[M]_D^{35°}$, of the compounds in different solvents is given in Table II. The sequence of their decreasing rotatory power is given below:

(*a*) *p-Aminobenzenesulphonylamido-2-thiazolecamphor-β-sulphonates.*—

Pyridine > Ethyl alcohol > Methyl alcohol > Water.

The sequence agrees with that of their dielectric constants but in the reverse order.

(*b*) *p-Sulphonamidophenyliminocamphors.*—

Chloroform > Pyridine > Acetone > Ethyl alcohol > Methyl alcohol.

The above order of decreasing rotatory power is exactly in the reverse order of their dielectric constants.

(*c*) *Camphor-β-sulphonylchlorides.*—

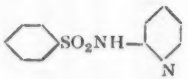
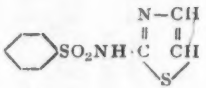
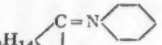
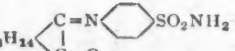
Pyridine > Methyl alcohol > Ethyl alcohol > Acetone > Chloroform > Benzene.

This order of decreasing rotatory power runs exactly parallel to the dielectric constants of the solvents except for pyridine which sometimes behaves abnormally.

(*d*) *Camphor-β-sulphonyl-α-pyridylamides.*—

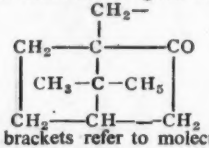
Acetone > Chloroform > Pyridine > Ethyl alcohol > Methyl alcohol.

TABLE II

No.	Structural formula	$[M]_D^{35°}$							
		Water (80)*	Methyl Alcohol (31·2)	Ethyl Alcohol (25·8)	Acetone (21·5)	Pyridine (12·4)	Chloroform (5·2)	Ether 4·3	Benzene (2·28)
1[c]	†R·SO_2H·H_2N [325][a]	66·64 (11·05)[b]	105·3 (20·43)	118·3 (22·74)	..	117·3 (24·60)	147·2 (30·15)	..	..
2[c]	R·SO_3H·H_2N [404]	68·57 (11·28)	113·2 (18·47)	..	..	135·2 (22·68)	..	..	..
3[d]	R·SO_3H·H_2N  [481]	..	96·18 (23·78)	108·2 (24·16)	120·2 (27·00)	..	..	..	..
4	R·SO_3H·H_2N·C  [487]	65·73 (14·61)	111·8 (24·12)	116·9 (25·33)	..	126·6 (27·29)	..	..	..
5[c]	C_8H_{14} [166]	..	113·6 (13·24)	164·7 (20·04)	180·7 (22·86)	..	175·1 (21·57)	168·2 (20·17)	180·4 (22·91)
6[c]	C_8H_{14}  [241]	..	1436 (265·4)	1489	1462 (282·2)	..	1597 (302·6)	1424 (265·60)	1622 (303·9)
7	C_8H_{14}  [320]	..	1074 (201·8)	1168 (218·5)	1202 (224·3)	1206 (225·3)	1250 (230·9)	.	..

	8[f]	$C_{10}H_{15}O\cdot SO_2\cdot OH$ [252]	55·94	..	..	..	..	91·64	..	..
A4	9	$C_{10}H_{15}O\cdot SO_2Cl$ [250·5]	..	119·0 (30·71)	98·95 (24·92)	87·68 (22·23)	124·0 (32·06)	80·16 (19·28)	..	71·39 (17·44)
	10[g]	$C_{10}H_{15}O\cdot SO_2Br$ [295]	..	..	..	..	..	76·6	..	..
	11[g]	$C_{10}H_{15}O\cdot SO_2NH_2$ [231]	..	..	..	..	..	3·465	..	..
	12[g]	$C_{10}H_{15}O\cdot SO_2NH$ [307]	..	..	..	..	..	206·5	..	..
	13	$C_{10}H_{15}O\cdot SO_2\cdot NH-$ [308]	..	107·2 (24·65)	110·9 (26·63)	141·7 (37·06)	123·2 (30·75)	127·8 (30·95)	..	..
	14	$C_{10}H_{15}O\cdot SO_2NH-$ [314]	..	109·9 (26·07)	117·7 (28·80)	149·1 (39·59)	130·3 (32·03)	138·1 (33·20)	..	..

* The values of dielectric constants are given in brackets.

† R= $C_{10}H_{15}O$ or 

[a] The values in square brackets refer to molecular weights.

[b] The values in brackets refer to molecular rotation constant, $\frac{M\times k}{100}$, in Drude's equation.

[c] The values of $\frac{M\times k}{100}$ for (1) & (2) are calculated from Singh, B. K., and Perti, O. N., *Proc. Ind. Acad. Sci.*, 1945, **22**, 8.

[d] The values of $\frac{M\times k}{100}$ for (3) is taken from Singh, B. K., and Manhas, K. M. S., *ibid.*, 1947, **26**, 61.

[e] The values of $\frac{M\times k}{100}$ for (5) & (6) are calculated from Singh, B. K., Mallik, H. P., and Bahaduri, B., *J. I. C. S.*, 1931, **8**, 6.

[f] The values are taken from Hilditch, T. P., *Jour. Chem. Soc.*, 1912, **101**, 192.

[g] The values for Nos. 10, 11 and 12 are taken from Armstrong, H. E. and Lowry, T. M., *ibid.*, 1902, **81**, 1441.

The sequence agrees with that of their dielectric constants in the reverse order except for acetone.

(*e*) *Camphor-β-sulphonyl-α-thiazoleamides.*—

Acetone > Chloroform > Pyridine > Ethyl alcohol > Methyl alcohol.

This sequence is again in the reverse order of their dielectric constants except for acetone.

Similar results follow if we compare the order of molecular rotation constants, K_0, with the dielectric constants of the solvents in which the dispersion of these compounds is observed. The values of k_0's are given in brackets (Table II).

As already pointed out in our previous work[1,3] it would, however, be more rational to compare the rotatory power of the solutions with their dielectric constants and not with the dielectric constants of the solvents.

The Effect of Substituent Groups on Rotatory Power

Rule[4] has shown that the arrangement of groups according to their polarities follows a general order with minor differences, whether the order is deduced from benzene substitution data, influence of various groups on dissociation constants of substituted acetic or benzoic acids or on the basis of electronic theory and that the order is

$\overline{OH}$, Cl, Br, I, NH_2, C_2H_5, CH_3, $\overset{+}{H}$, COOH, CHO, $COCH_3$, CN, $\overset{+}{NO_2}$

Table A

No.	Structural formula	$[\alpha]_D^{20°}$ in chloroform
I ..	$C_{10}H_{15}O\cdot SO_2\cdot OH$ (*a*)	39·47°
II ..	$C_{10}H_{15}O\cdot SO_2\cdot Cl$ (*b*)	32·0°
III ..	$C_{10}H_{15}O\cdot SO_2\cdot Br$ (*c*)	26·0°
IV ..	$C_{10}H_{15}O\cdot SO_2\cdot NH_2$ (*c*)	1·5°
V ..	$C_{10}H_{15}SO_2\cdot N$ (*c*)	−33·5°

(*a*) Hilditch, T. P., *Jour. Chem. Soc.*, 1912, **101**, 192.
(*b*) The present measurements were made at 35° C.
(*c*) Armstrong, H. E., and Lowry, T. M., *Jour. Chem. Soc.*, 1902, **81**, 1441.

In Table A the values of $[\alpha]_D^{20°}$ in chloroform of camphor-β-sulphonic acid and its four derivatives are given. On comparing these values of $[\alpha]_D^{20°}$, it is found that the order of rotatory power for the different substituents is OH > Cl > Br > NH_2 which runs exactly parallel to the above mentioned polar series.

THE RELATION BETWEEN CHEMICAL CONSTITUTION AND ROTATORY POWER

In Table II the molecular rotatory powers, $[M]_D^{35°}$, of 14 compounds in different solvents are given. The values of Drude's molecular rotation constants, $\frac{M \times k}{100}$, have also been included for the sake of comparison and are shown in brackets.

1. It is seen that the sulphathiazole salt (4) has higher rotatory power than the sulphapyridine salt (3). This supports our previous observation,[1] namely, that the thiazole ring has a higher rotatory effect than the pyridyl nucleus. A comparison of the values of $\frac{M \times k}{100}$ also bears out similar relationship.

2. (*a*) The replacement of an hydrogen atom of the phenyl group in the phenyliminocamphor (6) by $—SO_2NH_2$ group in *p*-sulphonamidophenyliminocamphor (7) depresses the rotatory power, whereas a similar replacement in anilinocamphor-β-sulphonate (1) increases the rotatory power in *p*-aminobenzene sulphonamido camphor-β-sulphonate (2).

(*b*) The values of the molecular rotation constants, $\frac{M \times k}{100}$ in organic solvents of two compounds (1 and 6, Table II) are depressed by substitution of an hydrogen atom by $—SO_2NH_2$ group (2 and 7, Table II) but are enhanced in water.

3. (*a*) The replacement of the hydroxy group in camphor-β-sulphonic acid (8) by Cl, Br and NH_2 (compounds numbered 9,10, 11, Table II) decreases the rotatory power in the order $Cl < Br < NH_2$. The depression of the rotatory power caused by the $—NH_2$ group (II) is phenomenal as the value of $[M]_D^{17°}$, in camphor-β-sulphonamide (11) in chloroform is as low as 3·5°.

(*b*) The replacement of an hydrogen atom in the SO_2NH_2 group of camphor-β-sulphonamide (11) by a phenyl radical (12) enhances the molecular rotatory power considerably from 3·5° to 206·5°. This effect, however, is less marked in pyridyl (13) and thiazole (14) derivatives (Table II).

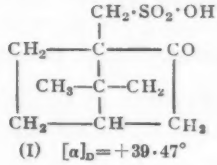
(*c*) It will be further observed that the thiazole derivative (14) has higher molecular rotatory power than the pyridyl compound (13) in agreement with the above mentioned observation on salts of camphor-β-sulphonic acids (Tables II, 3 and 4).

Similar results follow when a comparison is made of the values of molecular rotation constants, $\frac{M \times k}{100}$.

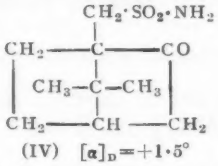
The Effect of Ring Structure on Rotatory Power

When an open chain optically active compound is transformed into a ring compound, there is a marked change in either sense, namely, an increase or decrease, in its rotatory power. The rotatory powers of the esters of 1-methyl-3-cyclopentanone-4-carboxylic acid are about thirty times as great as those of the corresponding methyl adipic esters.[5] Again the hexahydrophthalic acids have much lower rotatory power than their anhydrides.[6] On the other hand, ring formation may cause a great depression in rotatory power in some cases: camphoramic acids[7] have $[M]_D$ 89·45° (α), 119·4° (β) in ethyl alcohol, whilst their anhydride has $[M]_D$ 10·99°; camphoric acid[8] has $[M]_D$ 49·87° (1% ethyl alcohol solution), whereas its anhydride has $[M]_D$ 1·8°.

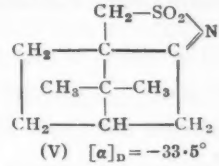
The replacement of the hydroxyl group of $-SO_2\cdot OH$ in camphor-β-sulphonic acid (I) by Cl and Br causes a progressively moderate decrease in rotatory power, but if the substituent group is NH_2 as in camphor-β-sulphonamide (IV), it produces a phenomenal depression (Table A):



(I) $[\alpha]_D = +39\cdot47°$

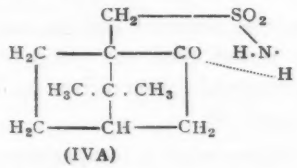


(IV) $[\alpha]_D = +1\cdot5°$



(V) $[\alpha]_D = -33\cdot5°$

The conversion of camphor-β-sulphonamide (IV) into camphor-β-sulphonanhydramide (V) is again accompanied by a great increase in rotatory power in the opposite sense. The decrease in the rotatory power of camphor-β-sulphonic acid by different substituents for the hydroxy group is in the following order: Cl < Br < NH_2. There is, however, a remarkably great depression in rotatory power in camphor-β-sulphonamide (IV), which may be due both to the nature of the substituent group ($-NH_2$) and to its close proximity to the carbonyl group—possibly bringing in hydrogen bonds into action forming a loosely closed structure (IV A) thus:



(IVA)

The structure postulated above (IV A) may account for the easy conversion of camphor-β-sulphonamide (IV) into camphor-β-sulphonanhydramide (V)

accompanied by a great change (increase) in rotatory power with ring closure.

Experimental

p-*Aminobenzenesulphonylamido-2-thiazole-camphor-β-sulphonates*

Molar proportions of *p*-aminobenzene sulphonylamido-2-thiazole and camphor-β-sulphonic acid (*d*-, *l*- or *dl*- form) were dissolved separately in absolute ethyl alcohol and ethyl acetate respectively. The two solutions were mixed and allowed to stand. The salt crystallised out on scratching the sides of the container. They were repeatedly recrystallised as white rectangular plates from a mixture of ethyl alcohol and ethyl acetate. These salts are fairly soluble in pyridine and methyl alcohol, less so in ethyl alcohol and water and practically insoluble in acetone, chloroform, benzene and ether. (Found: *d*-salt, m.p. 202° C.–204° C.; eq. wt. = 483·9, S = 20·09%, *l*-salt, m.p. 202° C.–204° C., eq. wt. = 487, S = 19·63%, *dl*-salt, m.p. 208° C.–210° C., eq. wt. = 487, S = 19·81%; $C_{19}H_{25}O_6S_3$ requires eq. wt. = 487, S = 19·7%.)

p-*Sulphonamido phenyl imino camphors*

Molar proportions of camphorquinone (*d*-, *l*- or *dl*-form) and *p*-aminobenzenesulphonamide (1·66 gm. and 1·72 gm. respectively) were ground together with anhydrous sodium sulphate (3 gm.). The mixture was suspended in absolute ethyl alcohol (10 c.c.) and refluxed on a water-bath for about six hours. On extraction with water, the compounds precipitated out. They were filtered, washed well with water and after repeated recrystallisations from dilute ethyl alcohol were obtained as yellow glistening rectangular plates. These compounds are fairly soluble in acetone, pyridine, methyl alcohol and chloroform, sparingly so in ethyl alcohol and practically insoluble in water, benzene and ether. The yield was about 2 grams. (Found *d*-salt, m.p. 228° C., S = 10·02%; *l*- salt, m.p. 228° C., S = 9·73%; *dl*-salt, m.p. 240° C., S = 10·12%; $C_{16}H_{20}N_2SO_3$ requires S = 10·00%.)

Camphor-β-sulphonylchlorides[9]

30 gm. of camphor-β-sulphonic acid (*d*-, *l*- and *dl*- form) were suspended in 60 c.c. of dry benzene in a round-bottomed flask and 30 c.c. of well cooled thionyl chloride was gradually added. The flask was fitted with a water condenser guarded with a calcium chloride tube and placed in an ice-bath for overnight. It was then refluxed on a water-bath till the unused camphor-β-sulphonic acid had dissolved. The excess of thionyl chloride was distilled off and then the excess of benzene was removed under reduced

pressure. The contents of the flask were then cooled and allowed to crystallise. They were filtered at the pump, washed with petroleum-ether and finally recrystallised as fine prisms out of petroleum-ether (animal charcoal). The mother liquor was also worked out to yield a further crop of crystals. The camphor-β-sulphonyl chlorides are soluble in pyridine, acetone, chloroform, benzene, ether, ethyl alcohol and methyl alcohol, very sparingly soluble in petroleum-ether and practically insoluble in water. The yield was about 15 gm. (Found: *d*-compound, m.p. 67° C., S = 12·63%; *l*-compound, m.p. 67° C., S = 12·69%; *dl*-compound, m.p. 72–74° C., S = 12·94%; $C_{10}H_{15}SO_3Cl$ requires S = 12·77%.)

Camphor-β-sulphonyl-α-pyridylamides

Molar amounts of camphor-β-sulphonyl chloride (*d*-, *l*- or *dl*-form), α-aminopyridine and pyridine were mixed together. The mixture was then refluxed for about 6 hours in an oil-bath at about 150° C. The resulting product in each case was then extracted with water, filtered and finally recrystallised as small rectangular plates from ethyl alcohol. It is fairly soluble in pyridine, chloroform and methyl alcohol, sparingly so in ethyl alcohol and acetone and practically insoluble in benzene, water and ether. (Found: *d*-compound, m.p. 208°–10° C., S = 10·33%; *l*-compound, m.p. 209°–10° C., S = 10·42%; *dl*-salt, m.p. 216°–18° C., S = 10·61%; $C_{15}H_{20}N_2SO_3$ requires S = 10·4%.)

Camphor-β-sulphonyl-α-thiazoleamides

Molar quantities of camphor-β-sulphonyl chloride (*d*-, *l*- or *dl*-form)-α-aminothiazole and pyridine were mixed together and refluxed in an oil-bath at about 150° C. for six hours. The resulting mass in each case was extracted with water, filtered and finally recrystallised as fine needles from ethyl alcohol. It is fairly soluble in pyridine and chloroform, less so in methyl alcohol, ethyl alcohol and acetone and practically insoluble in water, benzene and ether. (Found: *d*-compound, m.p. 238°–40° C., S = 20·57%; *l*-compound, m.p. 238°–40° C., S = 20·12%; *dl*-compound, m.p. 238–40° C., S = 20·49%; $C_{13}H_{18}N_2S_2O_3$ requires S = 20·4%.)

The rotatory power determinations were made in a 2-dcm. jacketed tube. The rotatory power determinations were carried out at approximately 35° C. The values of λ_0 calculated from the dispersion formulæ, are given in Tables III to VII and are expressed as μ or 10^{-4} cm.

TABLE III

p-Aminobenzenesulphonylamido-2-thiazolecamphor-β-sulphonates

Solvent		Water		Methyl alcohol		Ethyl alcohol		Pyridine	
Concentration in gm /100 c.c	*d*-	0·2500		1·0000		1·0000		1·0000	
	l-	0·2500		1·0000		1·0000		1·0000	
Calculated $[\alpha]_{\lambda_0}$		$\pm \frac{3{\cdot}001}{\lambda^2-0{\cdot}1328}$ 0·3644		$\pm \frac{4{\cdot}953}{\lambda^2-0{\cdot}1319}$ 0·3631		$\pm \frac{5{\cdot}203}{\lambda^2-0{\cdot}1304}$ 0·3611		$\pm \frac{5{\cdot}602}{\lambda^2-0{\cdot}1318}$ 0·3630	
Line		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
		d-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Li_{6708}	..	+ 8·00°	− 8·50°	+15·00°	−16·00°	+16·00°	−16·50°	+18·00°	−17·50°
Cd_{6438}	..	12·00	9·50	18·50	18·00	18·00	19·00	19·00	20·00
Li_{6104}	..	12·50	12·00	20·00	20·00	21·00	21·00	24·00	23·00
Na_{5893}	..	13·50	14·00	23·00	23·50	24·00	23·50	26·00	26·00
Hg_{5780}	..	14·00	15·00	24·50	24·00	26·00	25·00	27·50	28·00
Hg_{5461}	..	18·00	18·00	29·50	29·00	31·00	31·50	33·50	33·50
Ag_{5209}	..	22·00	22·00	36·00	35·00	37·00	36·50	41·00	40·50
Cd_{5086}	..	24·50	24·00	40·00	40·00	40·50	40·00	45·00	44·50
Cd_{4800}	..	32·00	31·50	51·50	50·00	52·50	52·50	56·00	56·00
Cd_{4678}	..	34·50	35·50	57·00	56·50	57·00	58·00	65·00	64·00
Li_{4603}	..	37·00	38·00	62·00	62·50	64·00	63·50	70·00	70·00
Hg_{4358}	..	54·50	50·60	87·50	86·00	89·00	88·50	100·00	98·00

TABLE IV

p-Sulphonamidophenyliminocamphors

Solvent		Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform	
Concentration in gm./100 c c.	*d-*	0·5000		0·2500		0·5000		0·5000		0·5000	
	l-	0·5000		0·2500		0·5000		0·5000		0·5000	
Calculated $[\alpha]$		$\pm \frac{63\cdot06}{\lambda^2 - \cdot1588}$		$\pm \frac{68\cdot28}{\lambda^2 - 0\cdot1581}$		$\pm \frac{70\cdot10}{\lambda^2 - 0\cdot1605}$		$\pm \frac{70\cdot26}{\lambda^2 - 0\cdot1617}$		$\pm \frac{72\cdot16}{\lambda^2 - 0\cdot1630}$	
Calculated λ_0		0·3985		0·3976		0·4006		0·4021		0·4037	
Line		Obs. [α]		Obs. [α]		Obs. [α		Obs. [α]		Obs. [α]	
		d-	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*
Li_{6708}	..	+216·5°	−217·8°	+233·6°	−236·4°	+240·5°	−241·3°	+243·8°	−241·8°	+251·7°	−250·6°
Cd_{6438}	..	245·0	248·6	263·7	268·8	279·8	277·7	278·6	276·3	287·3	287·7
Li_{6104}	..	293·4	293·1	319·9	320·2	331·6	332·0	331·8	334·8	342·5	243·5
Na_{5893}	..	335·6	335·9	365·1	258·6	375·8	374·2	376·9	376·7	390·6	392·2
Hg_{5780}	..	352·0	353·5	386·3	383·5	401·9	401·9	405·7	408·9	420·6	420·3
Hg_{5461}	..	451·8	451·3	487·3	485·7	509·0	506·8	514·6	515·2	534·5	532·0
Ag_{5209}	..	561·6	560·2	634·9	630·1	633·9	633·1	642·4	642·7	667·8	667·3
Cd_{5086}	..	632·7	630·1	679·5	679·9	714·4	715·1	..	..	..	..

TABLE V

Camphor-β-sulphonylchlorides

Solvent		Benzene		Chloroform		Acetone		Ethyl Alcohol		Methyl Alcohol		Pyridine	
Concentration in gm./100 c.c.	*d-*	0·5000		1·0000		1·0000		1·0000		1·0000		1·0000	
	l-	0·5000		1·0000		1·0000		1·0000		1·0000		1·0000	
Calculated $[\alpha]_{\lambda_0}$		$\pm \frac{6\cdot959}{\lambda^2-0\cdot1030}$ 0·3209		$\pm \frac{7\cdot697}{\lambda^2-0\cdot1010}$ 0·3178		$\pm \frac{8\cdot877}{\lambda^2-0\cdot0935}$ 0·3058		$\pm \frac{9\cdot95}{\lambda^2-0\cdot09543}$ 0·3089		$\pm \frac{12\cdot257}{\lambda^2-0\cdot08913}$ 0·2986		$\pm \frac{12\cdot796}{\lambda^2-0\cdot0888}$ 0·2980	
Line		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
		d-	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*
Li_{6708}	..	+19·50°	−21·00°	+23·00°	−23·00°	+24·00°	−24·50°	+28·50°	−27·50°	+32·00	−33·00°	+34·00°	−34·50°
Cd_{6438}	..	20·50	23·00	25·00	24·00	26·00	28·00	30·00	32·00	35·00	39·00	41·50	38·50
Li_{6104}	..	25·00	26·50	28·50	27·50	31·50	32·00	35·50	36·50	43·50	44·00	45·50	46·50
Na_{5893}	..	28·50	27·00	32·00	31·50	35·00	35·00	39·50	39·50	47·50	48·50	49·50	48·50
Hg_{5780}	..	30·50	28·50	33·50	34·00	37·50	37·50	42·00	41·50	50·00	50·50	52·00	53·00
Hg_{5461}	..	35·50	35·00	40·00	39·00	43·50	43·00	49·00	49·00	58·50	57·50	61·00	62·00
Ag_{5209}	..	40·00	43·00	44·00	44·00	50·00	49·00	57·00	57·50	68·50	66·50	72·00	71·50
Cd_{5086}	..	45·50	45·00	48·50	49·00	52·50	53·00	60·00	61·00	73·00	71·50	74·50	74·00
Cd_{4800}	..	55·00	52·50	58·50	59·00	63·50	65·00	74·50	74·00	87·50	86·00	92·00	92·00
Cd_{4678}	..	62·00	61·00	64·00	65·50	71·00	70·00	81·00	81·50	92·00	95·00	95·00	99·50
Li_{4603}	..	64·00	62·00	69·50	68·50	75·00	75·50	85·50	85·00	100·00	101·50	104·00	102·50
Hg_{4358}	..	82·00	78·50	85·00	87·00	90·00	91·00	107·00	107·00	120·00	123·00	124·50	124·00

TABLE VI

Camphor-β-sulphonyl-α-pyridylamides

Solvent		Methyl alcohol		Ethyl alcohol		Pyridine		Chloroform		Acetone	
Concentration in gm./100 c.c.	*d-*	0·2500		0·2500		1·0000		0·5000		0·2500	
	l-	0·2500		0·2500		1·0000		0·5000		0·2500	
Calculated $[\alpha]_{\lambda_0}$		$\pm \frac{8\cdot001}{\lambda^2-0\cdot1118}$ 0·3344		$\pm \frac{8\cdot645}{\lambda^2-0\cdot1071}$ 0·3273		$\pm \frac{9\cdot983}{\lambda^2-0\cdot09768}$ 0·3125		$\pm \frac{10\cdot049}{\lambda^2-0\cdot09721}$ 0·3118		$\pm \frac{12\cdot029}{\lambda^2-0\cdot08567}$ 0·2927	
Line		Obs. [α]		Obs. [α]		Obs [α]		Obs. [α]		Obs. [α]	
		d-	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*
Li_{6708}	..	+22·00°	−23·00°	+23·00°	−22·50°	+27·50°	−27·50°	+28·50°	−28·00°	+30·00°	−32·50°
Cd_{6438}	..	28·50	25·50	30·50	25·00	30·00	32·00	33·00	30·00	38·00	33·00
Li_{6104}	..	31·50	33·00	33·00	30·50	37·00	35·50	35·00	37·50	42·50	40·00
Na_{5893}	..	34·00	34·50	36·00	34·00	40·00	40·50	41·50	41·50	46·00	48·00
Hg_{5780}	..	35·50	35·00	38·50	40·00	41·50	41·50	44·00	44·00	50·00	50·00
Hg_{5461}	..	42·50	42·50	45·00	47·50	50·00	50·00	50·00	48·00	56·50	56·50
Ag_{5209}	..	52·50	53·00	50·00	50·00	58·50	58·00	56·00	56·00	60·50	66·50
Cd_{5086}	..	53·00	56·50	55·50	60·00	62·50	62·00	60·00	64·50	65·50	70·00
Cd_{4800}	..	69·00	68·50	69·00	72·50	75·00	76·50	..	..	80·00	80·00
Cd_{4678}	..	70·00	72·50	79·50	75·00	83·00	82·50	..	..	92·50	86·00
Li_{4603}	..	80·00	84·00	82·50	80·00	87·50	86·00	..	..	95·50	94·50
Hg_{4358}	..	100·50	104·50	108·00	107·50	..	..	..	..	120·00	118·50

TABLE VII

Camphor-β-sulphonyl-α-thiazoleamides

Solvent		Methyl alcohol		Ethyl alcohol		Pyridine		Chloroform		Acetone	
Concentration in gm./100 c.c.	*d*-	0·2500		0·2500		1·0000		0·5000		0·2500	
	l-	0·2500		0·2500		1·0000		0·5000		0·2500	
Calculated $[\alpha]_{\lambda_0}$		$\pm\frac{8\cdot304}{\lambda^2-0\cdot1098}$ 0·3314		$\pm\frac{9\cdot174}{\lambda^2-0\cdot1026}$ 0·3203		$\pm\frac{10\cdot202}{\lambda^2-0\cdot09819}$ 0·3133		$\pm\frac{11\cdot205}{\lambda^2-0\cdot08279}$ 0·2878		$\pm\frac{12\cdot612}{\lambda^2-0\cdot08162}$ 0·2857	
Line		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
		d-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Li_{6708}	..	+22·00°	−23·00°	+22·50°	−24·00°	+29·00°	−28·50°	+30·50°	−29·50°	+35·50	−33·00°
Cd_{6438}	..	30·50	31·00	30·00	26·00	31·50	31·50	32·00	34·50	36·00	39·50
Li_{6104}	..	32·00	32·50	32·00	34·00	37·50	38·00	36·50	38·50	42·50	45·00
Na_{5893}	..	35·00	35·00	37·50	37·50	41·50	41·00	44·00	42·00	47·50	50·00
Hg_{5780}	..	36·50	37·50	44·50	40·00	42·00	44·00	46·50	43·50	50·00	51·50
Hg_{5461}	..	44·00	44·00	47·00	47·00	51·00	51·50	52·00	53·50	55·00	58·00
Ag_{5209}	..	53·50	55·00	51·50	56·00	58·00	58·00	60·00	58·50	64·50	62·50
Cd_{5086}	..	51·50	57·50	55·00	62·00	..	..	..	..	73·50	70·00
Cd_{4800}	..	68·00	63·00	74·50	74·50	..	..	..	..	82·50	82·50
Cd_{4678}	..	80·00	73·50	76·00	80·50	..	..	..	..	90·00	93·50
Li_{4603}	..	81·50	78·00	84·00	83·00	..	..	..	..	97·00	97·00
Hg_{4358}	..	107·00	106·50	110·00	103·50	..	..	..	..	120·00	119·50

Summary

1. The rotatory dispersion of stereoisomeric compounds described in this paper is found in different solvents to obey the simple dispersion equation of Drude, $[\alpha] = \frac{K_0}{\lambda^2 - \lambda^2}$.

2. The equality of rotatory dispersions of dextro and lævo forms supports Pasteur's Law of Molecular Dissymmetry.

3. The effect of replacement of OH group in camphor-β-sulphonic acid by Cl, Br and NH_2 groups on rotatory power has been discussed and the polar effect of these groups on the rotatory power of the compounds also traced.

4. The effect of different solvents on the rotatory dispersion of the compounds described in this paper has been considered.

5. The thiazole group has a greater effect on rotatory power than the pyridyl nucleus.

6. The remarkably low rotatory power of camphor-β-sulphonamide is explained on the assumption of hydrogen bonds of the SO_2NH_2 group interacting with the oxygen atom of the carbonyl group.

Acknowledgement

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THE DIAMAGNETIC SUSCEPTIBILITIES OF PHTHALIC ACID AND PHTHALIC ANHYDRIDE

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In two previous communications[1,2] we have commented on the values of magnetic susceptibilities of camphoric and succinic acids and their respective anhydrides as recorded by Gray and Birse.[3] It was shown that the mean difference in the values of gram-molecular susceptibilities of optically active camphoric acids and their corresponding anhydrides was $-12{\cdot}95 \times 10^{-6}$ (as against -37×10^{-6} found by Gray and Birse)[3] and that the difference between the gram-molecular susceptibilities of succinic acid and its anhydride was $-13{\cdot}62 \times 10^{-6}$ (Gray and Birse found $-6{\cdot}92 \times 10^{-6}$). The differences found by us are, however, nearly equal to the gram-molecular susceptibility of water ($-12{\cdot}96 \times 10^{-6}$). These results are exactly in conformity with Pascal's additivity law and incidentally show that the earlier values of Gray and Birse[3] were erroneous.

We have further examined in this paper the cases of phthalic acid and its anhydride. Gray and Birse[3] found that the gram-molecular susceptibility of phthalic acid was $-81{\cdot}38$* and its anhydride, $-66{\cdot}01$. The difference ($-15{\cdot}37$) between the values of gram-molecular susceptibilities of phthalic acid and its anhydride is thus higher than that for the gram-molecular susceptibility of water ($-12{\cdot}96$). We have, therefore, repeated this work with carefully purified materials and find that the gram-molecular susceptibility of phthalic acid is $-81{\cdot}24$ and that of its anhydride $-67{\cdot}31$: The difference in these values comes to be $-13{\cdot}93$ which is about one unit higher than the gram-molecular susceptibility of water.

Experimental

Phthalic acid

Phthalic acid was prepared by oxidising naphthalene with concentrated sulphuric acid in the presence of mercuric sulphate as a catalyst.[4] It was purified by repeated crystallisations from hot water when it was obtained as short prisms, m.p. 213° C.

* The unit of magnetic susceptibility is taken throughout this paper as 10^{-6} c. g. s. e. m. u.

Phthalic anhydride

Phthalic anhydride was obtained by heating phthalic acid in a sublimation apparatus. The sublimate which consisted of long needles was pure anhydride, m.p. 128° C.

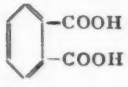
The measurements of magnetic susceptibility were carried out on a modified type of Guoy's Balance. The working of the balance was checked by making determinations of magnetic susceptibilities of compounds with known values. Special care was taken in the purification of the substances used in these measurements, particularly in avoiding their contamination with any paramagnetic impurity. The compounds were carefully dried in vacuum for several days before use. The results of these measurements are recorded in Table I.

TABLE I

Substance	m. p.	$-\chi \times 10^6$ (per gram)	$-\chi_M \times 10^6$ (per gram molecule)	$-\chi_M \times 10^6$ (Gray and Birse[4])
Phthalic acid ..	213°	0·4894	81·24	81·38
Phthalic anhydride ..	128°	0·4548	67·31	66·01
Difference ..			13·93	15·37

DISCUSSION

We now illustrate the values given in the above mentioned measurements (Table I) by calculating the gram-molecular susceptibilities of phthalic acid and phthalic anhydride using Pascal's corrected values for susceptibility constants and constitutive correction constants (λ) as follows:

1. Phthalic acid, ($C_8H_6O_4$), 

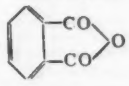
(i) Atomic Susceptibilities:

8 Carbon atoms	$= -6{\cdot}00 \times 8 = -48{\cdot}00$
6 Hydrogen atoms	$= -2{\cdot}93 \times 6 = -17{\cdot}58$
2 [= O]	$= -3{\cdot}36 \times 2 = -6{\cdot}72$
2 [− O −]	$= -4{\cdot}61 \times 2 = -9{\cdot}22$

(ii) Constitutive correction constants (λ)

one benzene nucleus	$= -1{\cdot}44 \times 1 = -1{\cdot}44$
Calculated value ..	$= -82{\cdot}96$
Experimental value (Table I) ..	$= -81{\cdot}24$
Percentage deviation	$= 2{\cdot}07$

The diamagnetic contribution of the two quaternary carbon atoms on the two functional groups containing oxygen $\left(-C\begin{matrix}O\\OH\end{matrix}\right)$ cancels out on account of their symmetrical position with regard to the phenylene group.

2. Phthalic anhydride, $C_8H_4O_3$, 

(i) Atomic susceptibilities:

8 Carbon atoms	.. ..	$= -6.00 \times 8 = -48.00$
4 Hydrogen atoms	.. ..	$= -2.93 \times 4 = -11.72$
2 [= O]	.. .. ..	$= -3.36 \times 2 = -6.72$
1 [– O –]	.. .. ..	$= -4.61 \times 1 = -4.61$

(ii) Constitutive correction constant (λ)

one benzene nucleus	.. ..	$= -1.44 \times 1 = -1.44$
Calculated value	..	$= -72.49$

There is no constitutive correction for oxygen due to symmetry.

Experimental value (Table I) .. $= -67.31$

The difference between the calculated and experimental values ($+5.18$) must be attributed to the ring structure of phthalic anhydride.

The observed difference in the gram-molecular susceptibilities of dibasic acids and their anhydrides are given in Table II.

TABLE II

	$-\chi_M \times 10^6$	Difference
Camphoric acid[1] ..	125·20	12·95
Camphoric anhydride[1] ..	112·25	
Succinic acid[2] ..	57·47	13·62
Succinic anhydride[2] ..	43·85	
Phthalic acid ..	81·24	13·93
Phthalic anyhydride ..	67·31	

It will be observed that the difference between the susceptibilities of dicarboxylic acids and their corresponding anhydrides (Table II) is nearly equal to (-13), the gram-molecular susceptibility of water. This is in exact accordance with Pascal's law as these anhydrides are formed from the acids by the loss of a molecule of water.

CONSTITUTIVE CORRECTION CONSTANT FOR WATER

The observed gram-molecular susceptibility of water is -12.96, whereas on Pascal's additivity law, it should be -10.47. The difference (-2.49) is thus the constitutive correction constant (λ) for a gram-molecule of water.

In Table III, the paramagnetic effects of the 5- and 6-membered rings are shown.

TABLE III

Name of the anhydride	Contribution due to the heterocyclic ring
Camphoric anhydride (6-membered)[2] ..	+ 2·61
Succinic anhydride (5-membered)[2] ..	+ 3·21
Phthalic anhydride (5-membered) ..	+ 5·18

The 6-membered ring in camphoric anhydride contains a *gem*-dimethyl group; it is, therefore, under the least strain. The 5-membered anhydride ring in phthalic anhydride would appear to be under the greatest strain on account of its conjugation with a benzene ring. The 5-membered ring in succinic anhydride would occupy an intermediate position. The paramagnetic effects of the different rings given in Table III are thus qualitatively proportional to the strain in them.

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SUMMARY

1. The gram-molecular susceptibilities of carefully purified samples of phthalic acid and its anhydride are determined.

The susceptibilities are:

Phthalic acid, χ_M .. .. $= -81{\cdot}24 \times 10^{-6}$

Phthalic anhydride, χ_M.. .. $= -67{\cdot}31 \times 10^{-6}$

It is found that whereas the value of the gram-molecular susceptibility of phthalic acid found by Gray and Birse and ourselves is nearly equal, that for the anhydride is higher in our case.

2. The difference in gram-molecular susceptibilities of dibasic acids and their anhydrides is nearly equal to that of water with minor variations, possibly due to different structures attached to the anhydride rings.

3. The constitutive effect of the rings in the anhydrides of different dibasic acids has also been discussed.

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